Electronic Supporting Information

Part I: Experimental Details

"Size-Dependent Rate Acceleration in the Silylation of Secondary Alcohols: the Bigger the Faster"

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1. Supplementary Data of Competition Experiments

1.1. Supplementary Figures

Figure S1 shows the set of alcohols and silyl chlorides, that was chosen to investigate both, the influence of repulsive and attractive steric effects in this study. The goal of this choice is to monitor the interplay of the repulsive and the attractive part of van-der-Waals-forces in aromatic stacking. Mainly looking at symmetric silyl chlorides allows to presume a certain interplay of at least one surface of the silyl chloride with the alcohol. Nevertheless, also two asymmetric silyl chlorides were investigated to see the influence of a mixed set of moieties on the Si-atom.

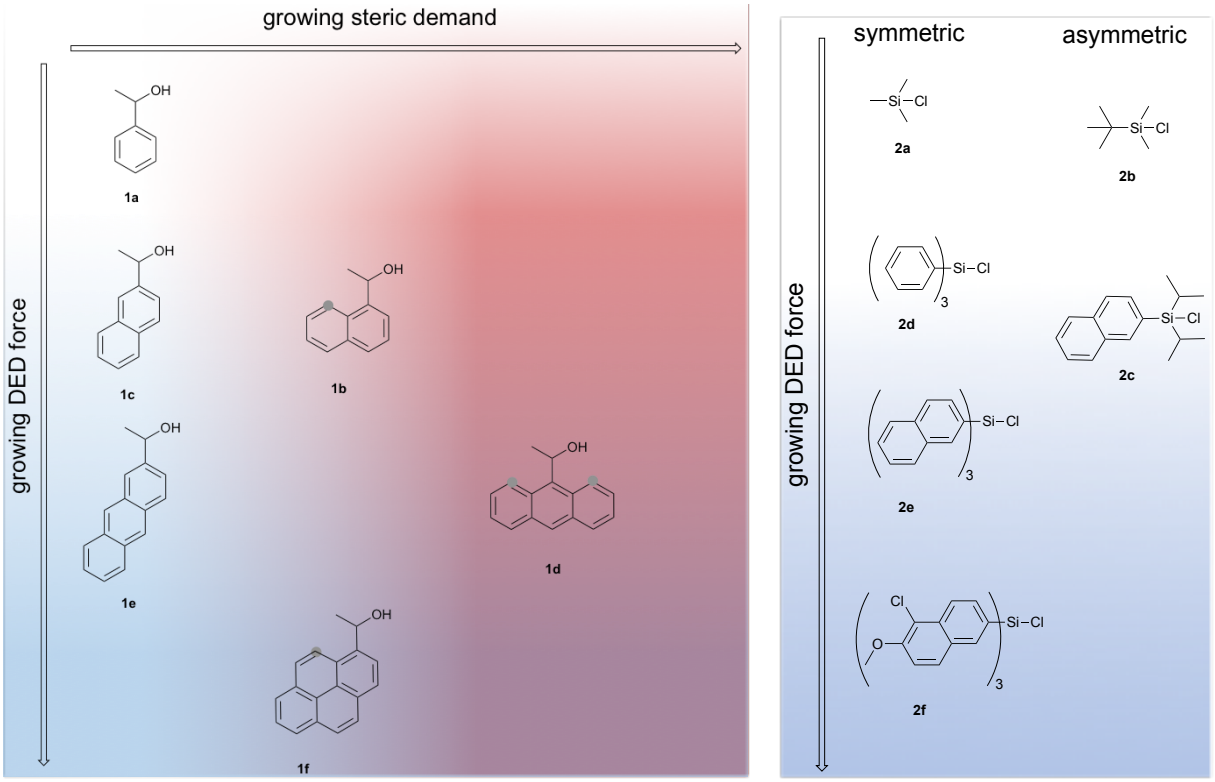


Figure S1: Set of investigated alcohols and silyl chlorides shown in dependence of their DED force and steric demand.

In Figure S2 the relative rate-constants for each alcohol are plotted depending on the used silyl chloride. In this graph it becomes very clear, that increasing the size of the moieties of the silyl chlorides accelerates the reaction for every investigated alcohol. The relative rate-constant values and associated standard deviations can be found from Table S1 to Table S5.

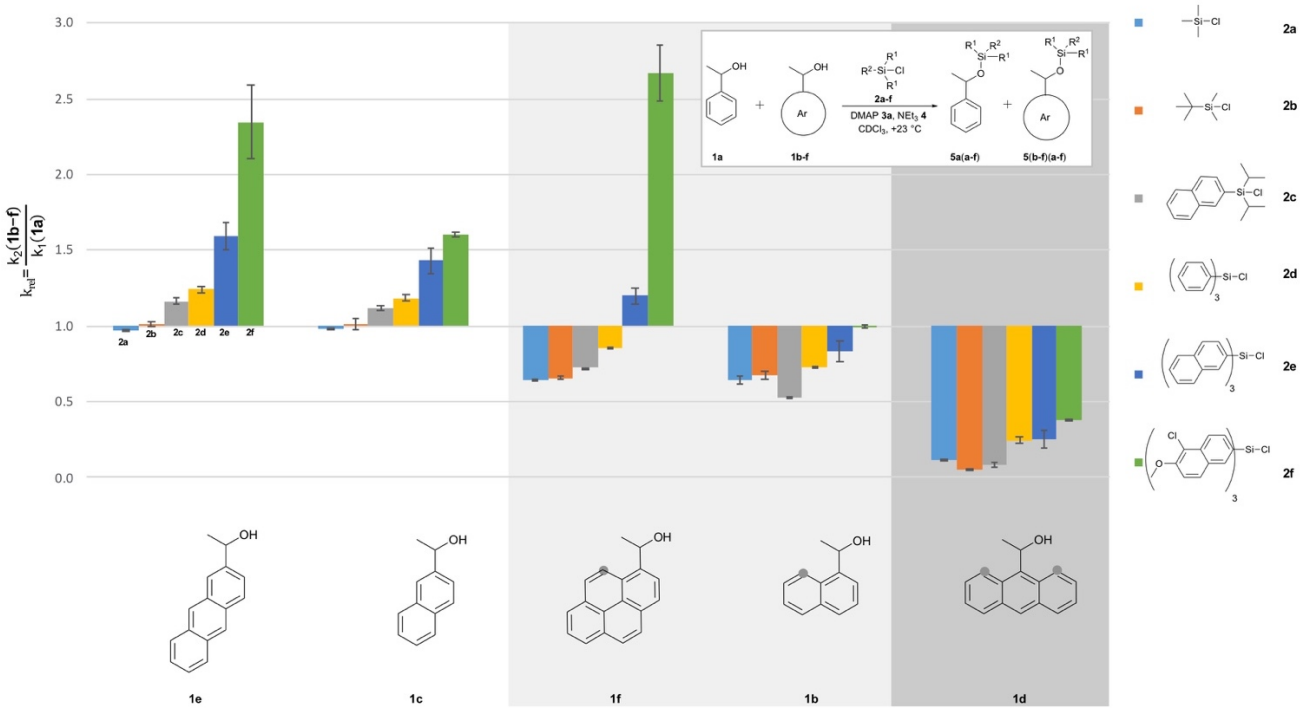
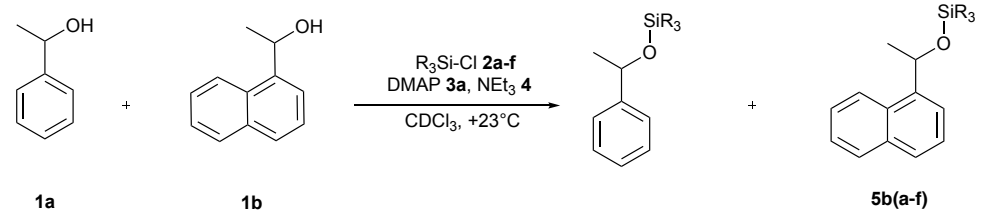


Figure S2: Relative rate constants for the silylation of alcohols depending on the size of the silyl chloride. Grey coloured areas indicate the sterically hindrance for those alcohols.

1.2. Table of Competition Experiments Results

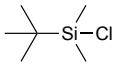
Table S1: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for competition experiments with alcohol **1a** and **1b**.



1a **1b** **5b(a-f)**

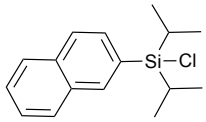
2a

Conversion (%)	*Chemo-selectivity*
13.865	-0.175
30.233	-0.191
45.045	-0.166
59.426	-0.145
77.949	-0.096
k_{rel}	
0.640±0.024	



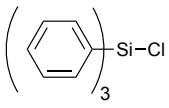
2b

Conversion (%)	*Chemo-selectivity*
21.171	-0.159
31.687	-0.170
44.829	-0.155
64.470	-0.125
71.212	-0.085
k_{rel}	
0.673±0.030	



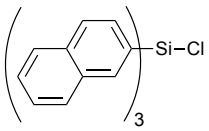
2c

Conversion (%)	*Chemo-selectivity*
22.368	-0.277
29.169	-0.272
41.438	-0.242
55.379	-0.206
67.642	-0.169
k_{rel}	
0.523±0.005	



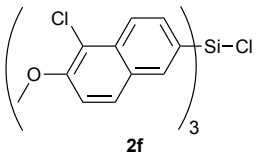
2d

Conversion (%)	*Chemo-selectivity*
19.894	-0.140
33.497	-0.128
46.740	-0.120
61.058	-0.094
75.264	-0.073
k_{rel}	
0.726±0.006	



2e

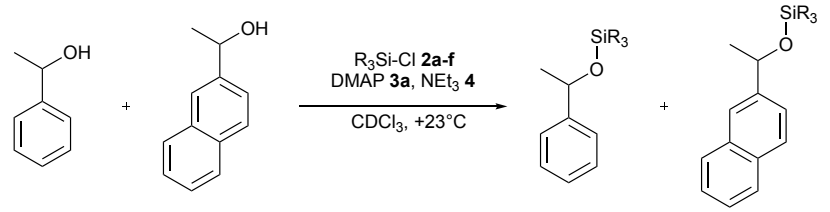
Conversion (%)	*Chemo-selectivity*
15.553	-0.134
30.387	-0.097
44.963	-0.070
58.394	-0.048
74.354	-0.018
k_{rel}	
0.829±0.068	



2f

Conversion (%)	*Chemo-selectivity*
17.325	-0.002
26.192	0.003
39.763	-0.004
52.723	-0.003
66.018	0.001
k_{rel}	
0.998±0.008	

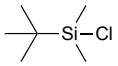
Table S2: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for competition experiments with alcohol **1a** and **1c**.



1a **1c** **5a(a-f)** **5c(a-f)**

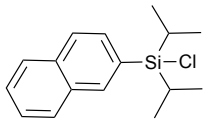
2a

Conversion (%)	*Chemo-selectivity*
23.509	-0.009
32.827	-0.008
53.343	-0.008
64.271	-0.007
75.116	-0.007
k_{rel}	
0.977±0.003	



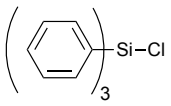
2b

Conversion (%)	*Chemo-selectivity*
18.845	0.028
31.894	-0.001
46.448	-0.010
58.237	0.003
74.006	0.195
k_{rel}	
1.010±0.038	



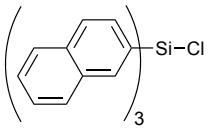
2c

Conversion (%)	*Chemo-selectivity*
25.520	0.056
29.814	0.044
43.240	0.045
56.938	0.033
62.470	0.030
k_{rel}	
1.119±0.014	



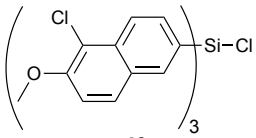
2d

Conversion (%)	*Chemo-selectivity*
21.114	0.088
32.374	0.072
50.573	0.048
63.154	0.051
74.976	0.037
k_{rel}	
1.186±0.026	



2e

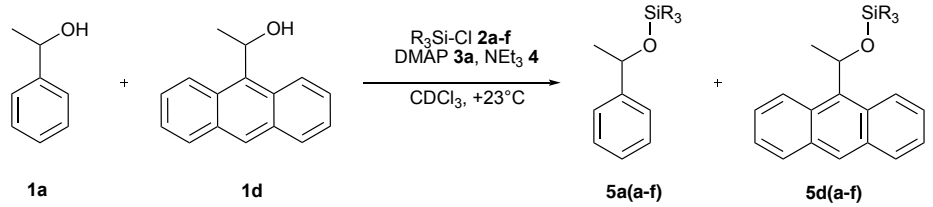
Conversion (%)	*Chemo-selectivity*
21.703	0.120
23.765	0.145
36.611	0.137
51.650	0.134
64.604	0.120
k_{rel}	
1.430±0.083	



2f

Conversion (%)	*Chemo-selectivity*
22.791	0.204
27.153	0.202
38.102	0.177
53.053	0.157
64.738	0.129
k_{rel}	
1.599±0.015	

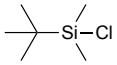
Table S3: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for competition experiments with alcohol **1a** and **1d**.



1a **1d** **5a(a-f)** **5d(a-f)**

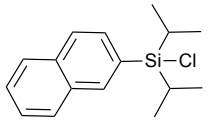
2a

Conversion (%)	*Chemo-selectivity*
20.269	-0.750
31.347	-0.724
48.222	-0.658
59.346	-0.573
75.734	-0.338
k_{rel}	
0.114±0.004	



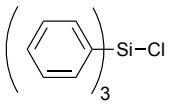
2b

Conversion (%)	*Chemo-selectivity*
20.057	-0.860
31.861	-0.863
45.977	-0.834
58.883	-0.713
62.807	-0.624
k_{rel}	
0.051±0.008	



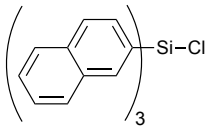
2c

Conversion (%)	*Chemo-selectivity*
13.552	-0.789
25.449	-0.809
42.558	-0.762
51.304	-0.734
60.546	-0.652
k_{rel}	
0.082±0.016	



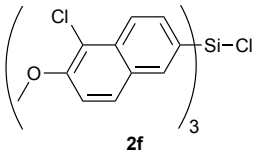
2d

Conversion (%)	*Chemo-selectivity*
19.594	-0.528
30.339	-0.571
52.660	-0.446
61.251	-0.402
76.578	-0.261
k_{rel}	
0.242±0.021	



2e

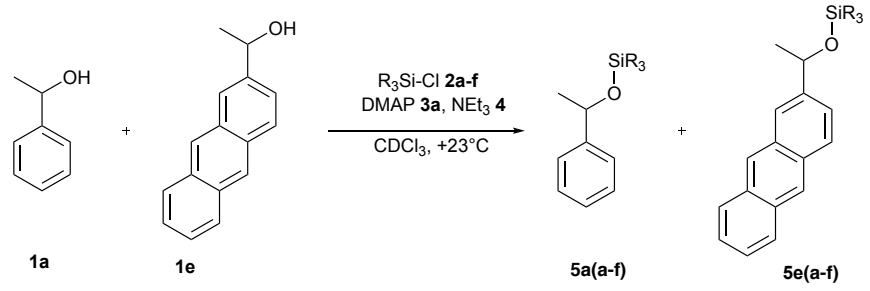
Conversion (%)	*Chemo-selectivity*
16.714	-0.645
30.345	-0.594
45.458	-0.478
59.555	-0.363
75.326	-0.228
k_{rel}	
0.251±0.061	



2f

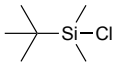
Conversion (%)	*Chemo-selectivity*
16.423	-0.410
30.392	-0.388
42.903	-0.358
52.231	-0.309
57.650	-0.296
k_{rel}	
0.380±0.008	

Table S4: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for competition experiments with alcohol **1a** and **1e**.



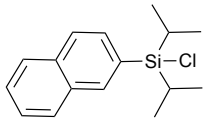
2a

Conversion (%)	*Chemo-selectivity*
21.353	-0.015
33.088	-0.011
49.509	-0.011
64.805	-0.008
79.547	-0.006
k_{rel}	
0.970±0.003	



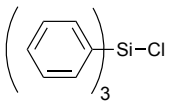
2b

Conversion (%)	*Chemo-selectivity*
15.479	0.007
28.281	0.011
40.967	0.000
55.161	-0.002
66.235	0.004
k_{rel}	
1.010±0.013	



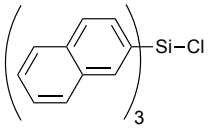
2c

Conversion (%)	*Chemo-selectivity*
12.745	0.061
14.871	0.082
25.390	0.062
34.317	0.062
46.925	0.050
k_{rel}	
1.161±0.021	



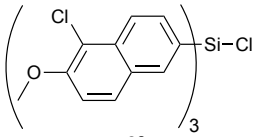
2d

Conversion (%)	*Chemo-selectivity*
28.007	0.099
33.300	0.096
48.936	0.072
61.764	0.061
75.547	0.045
k_{rel}	
1.241±0.022	



2e

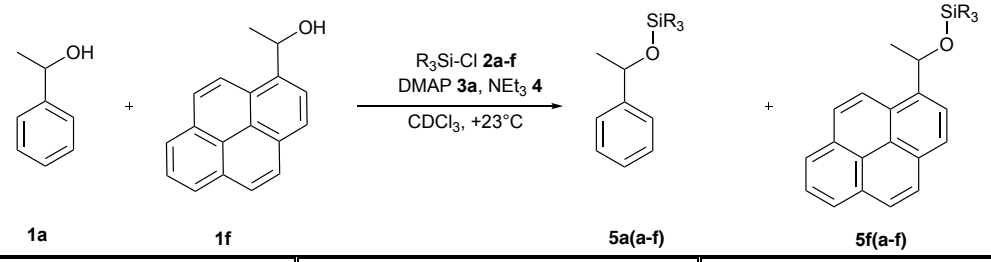
Conversion (%)	*Chemo-selectivity*
14.650	0.169
23.847	0.190
37.639	0.190
50.214	0.176
63.484	0.144
k_{rel}	
1.592±0.092	



2f

Conversion (%)	*Chemo-selectivity*
17.612	0.411
32.237	0.361
49.407	0.299
65.953	0.210
78.651	0.140
k_{rel}	
2.344±0.243	

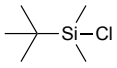
Table S5: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for competition experiments with alcohol **1a** and **1f**.



1a **1f** **5a(a-f)** **5f(a-f)**

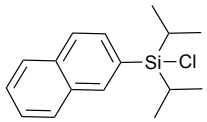
2a

Conversion (%)	*Chemo-selectivity*
22.909	-0.191
32.226	-0.183
46.926	-0.157
61.981	-0.130
77.344	-0.094
k_{rel}	
0.642±0.003	



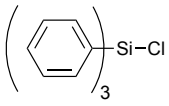
2b

Conversion (%)	*Chemo-selectivity*
22.056	-0.177
31.809	-0.172
44.500	-0.153
63.723	-0.122
75.076	-0.103
k_{rel}	
0.654±0.011	



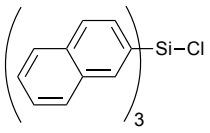
2c

Conversion (%)	*Chemo-selectivity*
13.686	-0.145
28.209	-0.136
40.559	-0.125
55.836	-0.103
62.950	-0.096
k_{rel}	
0.722±0.004	



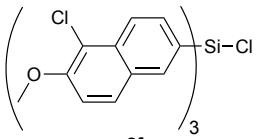
2d

Conversion (%)	*Chemo-selectivity*
20.342	-0.069
32.896	-0.069
48.088	-0.055
64.070	-0.045
76.392	-0.039
k_{rel}	
0.850±0.007	



2e

Conversion (%)	*Chemo-selectivity*
17.691	0.054
28.697	0.074
45.279	0.066
59.617	0.058
73.404	0.057
k_{rel}	
1.199±0.051	



2f

Conversion (%)	*Chemo-selectivity*
14.989	0.451
27.020	0.405
40.279	0.370
53.006	0.319
70.551	0.211
k_{rel}	
2.674±0.184	

2. Experimental Determination of Relative Rate Constants

2.1. Experimental Methodology of Competition Experiments

Technical Details

For the competition experiments the stringent adherence to the protocol is vital. All experimental equipment, including calibrated flasks, NMR-tubes, gas chromatography vials (GC-vials), magnetic stir bars, was dried in the oven at 110°C overnight prior to use. All Hamilton syringes were cleaned with acetone, dried under vacuum, and flushed with nitrogen.

The GC-vial holder (Shimadzu 221-44998-91) was connected to the circuit of a cryostat maintaining +23 °C (noted temperatures, resp.) constantly and placed on a magnetic stirrer. The speed of stirring was fixed at 750 rpm for all the experiments described in the following.

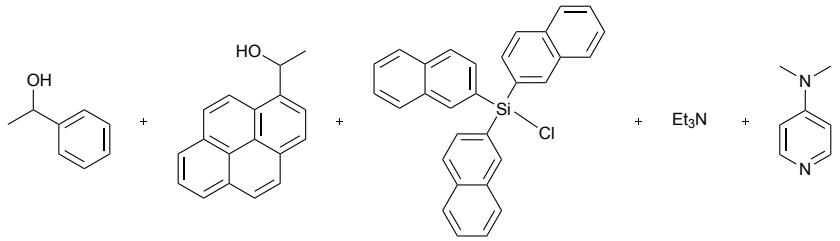
Preparation of Stock Solutions

Calibrated flasks of various sizes (1 mL, 2 mL, 5mL, 10 mL and 20 mL) are placed in a Schlenk flask and evacuated and purged with N_2 for three times. The compounds are weighed in and the solvent is applied via Hamilton syringe under N_2 –atmosphere in the same Schlenk flask. The finished stock solutions are kept in a nitrogen-filled exsiccator until employed. A guideline for the preparation of the stock solutions is shown as follows in a representative example for a competition experiment.

Table S6: Composition of stock solutions for competition experiments.

name of stock solution	compounds in stock solution
Stock A	1:1 – mixture of alcohol **1a** and competing alcohol
Stock B	silyl chloride (conc. regarding both alcohols in%)
B_1	20%
B_2	35%
B_3	50%
B_4	65%
B_5	80%
Stock C	Catalyst (conc. reg. both alcohols in%) + Et_3N (1.15 eq reg. both alcohols)

Representative Example



1a **1f** **2e** **4** **3a**

Scheme S1: Example of a competition experiment with alcohols **1a** and **1f**, silylation agent 2e, catalyst DMAP **3a** and triethylamine **4**.

In the following example seven stock solutions have to be prepared under nitrogen. All percentages and equivalents are regarding the concentration of both alcohols together (0.2 M). Stock A contains the alcohols **1a** and **1f** in a concentration of 0.1 M each. Stock solutions B_1 to B_5 contain the silyl chloride **2e** in different concentrations (20%, 35%, 50%, 65% and 80% of 0.2 M). Stock solution C contains the catalyst **3a** (0.09 M, 15%) and triethyl amine **4** (1.17 eq).

Table S7: Preparation of Initial Stock Solutions for competition experiments.

		c [mol/l]	Vol. Flask [mL]	*N* [mmol]	M.W	*m* [mg]
Stock A	1a	0.10	10.00	1.00	122.17	122.17
	1f	0.10	10.00	1.00	222.29	222.29
Stock B_1 (20%)	2e	0.04	2.00	0.08	445.03	35.60
Stock B_2 (35%)	2e	0.07	2.00	0.14	445.03	62.30
Stock B_3 (50%)	2e	0.10	2.00	0.20	445.03	89.01
Stock B_4 (65%)	2e	0.13	2.00	0.26	445.03	115.71
Stock B_5 (80%)	2e	0.16	2.00	0.32	445.03	142.41
Stock C	3a	0.23	10.00	2.30	101.19	232.74
	4 (15%)	0.03	10.00	0.30	122.17	36.65

Preparation of the GC-vials

An oven dried empty GC-vial is transferred to a Schlenk flask. The Schlenk flask containing the vial and the cap is three times evacuated and flushed with nitrogen. Now 0.5 mL of the stock solutions are transferred in the GC-vial via a Hammilton-type syringe

in the order A (mixture of alcohols), C (catalyst **3** and triethylamin **4**) and B_x (silyl chloride in the corresponding concentration). Then, the GC-vial is capped under nitrogen and placed quickly in the tempered GC-vial and stirred at 750 rpm for the stated time.

Preparation of the NMR-Samples

The reaction is monitored by ^{1}H-NMR of the sample with the highest concentration of Silylation agent.

An oven dried NMR tube is evacuated and flushed with N_2 three times. The caped GC-vial containing the reaction mixture is placed in a special Schlenk flask and evacuated and vented three times with N_2. Now, 0.6 mL of the reaction solution is transferred via syringe into the NMR-tube, caped and sealed with Parafilm©.

The NMR spectrum is measured using a 600 MHz NMR machine.

2.2. Determination of Relative Rate Constants from Experimental Results

Analysis of the ^{1}H-NMR Spectra

^{1}H-NMR spectra are processed using MestReNova©. Automated phase correction and a Bernstein polynomial fit with polynomial order 3 are applied, the spectra is referenced by the $CDCl_3$ solvent signal (7.26 ppm).

If possible the α-hydrogen signal of the two alcohols and the two silyl ethers is integrated in each of the spectra. If those signals are overlapping, the corresponding methane-signal is used instead.

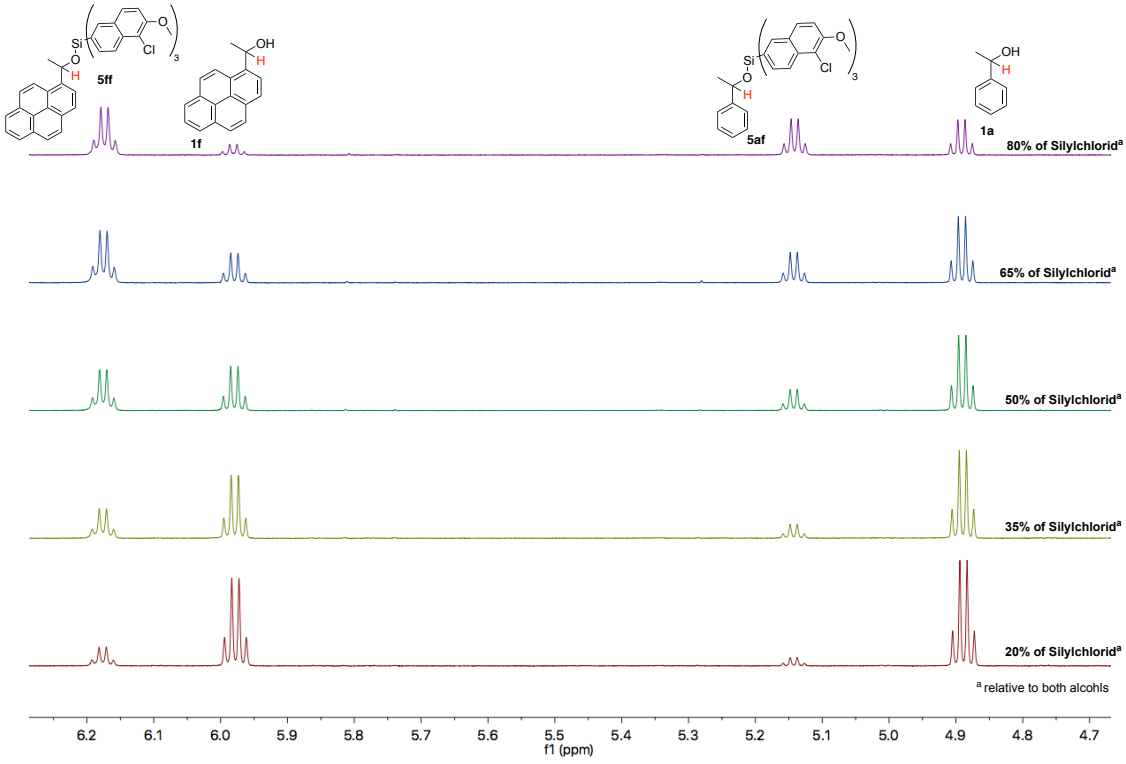
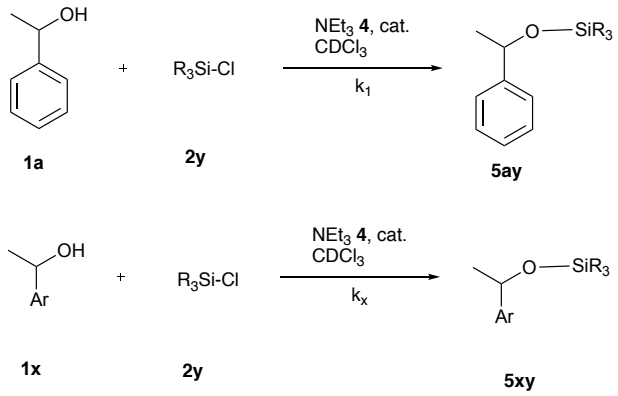


Figure S3: Representative example of stacked spectra with the relevant signals.

Calculation of Chemoselectivity, Conversion and Relative Rate Constant



Scheme S2: General equation of the competing reactions.

As we were able to rule out that after the end of the reaction the product ratio is varied through thermodynamic processes (compare SI chapter 4.2), relative rate constants can be calculated from the product ratios. Relative rate constants are defined similarly to selectivity *S* depending on the rate constant for the silylation of 1-phenylethanol **1a** as shown in Eq. S1.

$$S = k_{rel} = \frac{k_x}{k_1} = \frac{k_{(\mathbf{1x}+\mathbf{2y})}}{k_{(\mathbf{1a}+\mathbf{2y})}} \quad \text{Eq. S1}$$

In order to determine the selectivity, the chemoselectivity and the conversion is needed. The exact conversion is calculated by Eq. S2, whereby the integrals of the ^{1}H-NMR spectra are used to determine concentrations.

$$conversion\ [\%] = \left(\frac{[\mathbf{5ay}]\ + [\mathbf{5xy}]}{[\mathbf{1a}] + [\mathbf{1x}] + [\mathbf{5ay}]\ + [\mathbf{5xy}]}\right) \cdot\ 100 \quad \text{Eq. S2}$$

Regarding the definition of selectivity in Eq. S1, the experimental chemoselectivity C_{exp} is defined by Eq. S3.

$$C_{exp}\ = \frac{[\mathbf{5xy}]\ - [\mathbf{5ay}]}{[\mathbf{5xy}] + [\mathbf{5ay}]} \quad \text{Eq. S3}$$

This definition of C_{exp} presumes an exact 1:1 ratio of both reactants **1a** and **1x**. To eliminate errors from small deviations of this ratio due to unavoidable experimental inaccuracies, a correction factor is introduced, that calculates the actual initial ratio of both reactants by Eq. S4.

$$f = \frac{[\mathbf{1x}]_0}{[\mathbf{1a}]_0} = \frac{[\mathbf{1x}]\ + [\mathbf{5xy}]}{[\mathbf{1a}]\ + [\mathbf{5ay}]} \quad \text{Eq. S4}$$

The effective chemoselectivity *C* can then be calculated as

$$C\ = \frac{[\mathbf{5xy}]\ - [\mathbf{5ay}] \cdot f}{[\mathbf{5xy}] + [\mathbf{5ay}] \cdot f} \quad \text{Eq. S5}$$

In this paper, we always use this effective chemoselectivity *C*. Having the chemoselectivity *C* and the conversion in hand, the selectivity *S*, which corresponds to the relative rate constant, can be calculated by Eq. S6.[1] The stated numbers are the average of five experiments with various amounts (20%, 35%, 50%, 65%, 80% of both alcohols) of silyl chlorides.

$$k_{rel} = S\ = \frac{\ln\,(1 - conv(1 + C))}{\ln\,(1 - conv(1 - C))} \quad \text{Eq. S6}$$

2.3. Table of Integrals of Competition Experiments

Table S8: Integral regions and relative integral values for competition experiments of alcohol **1a** and alcohol **1b-f** using silyl chloride **2a-f**. Alcohol **1a** is highlighted in green, corresponding silyl ether **5a(a-f)** in red, the competing alcohol **1(b-f)** in yellow and its corresponding silyl ether **5(b-f)(a-f)** in blue.

alc	Si-Cl	% Si-Cl	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral
1b	**2a**	20%	1.68114	1.64657	1.00000	1.59666	1.57170	0.12797	1.50624	1.47494	1.03444	1.43853	1.41439	0.19952
1b	**2a**	35%	1.68012	1.64310	1.00000	1.59441	1.56822	0.31954	1.50379	1.47065	0.93756	1.44139	1.40948	0.52008
1b	**2a**	50%	1.67501	1.65128	1.00000	1.59154	1.56168	0.59309	1.50154	1.47310	0.85549	1.43792	1.40396	0.92777
1b	**2a**	65%	1.67439	1.64657	1.00000	1.59298	1.56066	1.01752	1.49581	1.47126	0.72700	1.43607	1.40150	1.51195
1b	**2a**	80%	1.67501	1.64310	1.00000	1.58725	1.55881	2.34281	1.50051	1.46778	0.56634	1.43321	1.39864	3.19412
1b	**2b**	20%	1.65038	1.61854	1.00000	1.56685	1.54148	0.21744	1.47716	1.44782	0.88712	1.40115	1.37483	0.28937
1b	**2b**	35%	1.64341	1.61701	1.00000	1.55794	1.53677	0.35706	1.47153	1.44542	0.84781	1.39310	1.36888	0.50007
1b	**2b**	50%	1.64051	1.61201	1.00000	1.55218	1.52401	0.61232	1.46647	1.44027	0.74929	1.38666	1.35915	0.80907
1b	**2b**	65%	1.63190	1.60540	1.00000	1.53924	1.51205	1.29735	1.46074	1.43457	0.62112	1.37385	1.34768	1.64420
1b	**2b**	80%	1.62242	1.58164	1.00000	1.53577	1.49202	1.86103	1.45136	1.41132	0.68587	1.36682	1.32355	2.30936
1b	**2c**	20%	5.81096	5.75661	1.00000	5.69981	5.64973	5.12498	5.06039	5.01397	1.64496	4.91565	4.86740	4.05470
1b	**2c**	35%	5.80608	5.75966	1.00000	5.70348	5.64851	3.66054	5.06711	5.01214	1.62470	4.91748	4.86068	2.71310
1b	**2c**	50%	5.80608	5.75478	1.00000	5.70348	5.65340	2.15760	5.06039	5.01214	1.52608	4.91565	4.87045	1.41230
1b	**2c**	65%	5.80608	5.75478	1.00000	5.70348	5.65157	1.26254	5.06039	5.01092	1.43944	4.91870	4.86923	0.70302
1b	**2c**	80%	5.80608	5.75295	1.00000	5.70653	5.65645	0.77089	5.05917	5.01092	1.33504	4.92236	4.87045	0.34615
1b	**2d**	20%	5.79571	5.73119	1.00000	5.67858	5.59474	4.80838	5.05304	4.98851	1.22034	4.89357	4.81713	4.13208
1b	**2d**	35%	5.79217	5.73196	1.00000	5.67065	5.60823	2.40955	5.05164	4.98811	1.20965	4.88839	4.82707	1.97735
1b	**2d**	50%	5.79015	5.73086	1.00000	5.67572	5.61340	1.42143	5.05067	4.98684	1.19502	4.89507	4.83464	1.07979

1b	**2d**	65%	5.78763	5.73186	1.00000	5.67941	5.61699	0.80172	5.04599	4.98800	1.13362	4.89493	4.83805	0.55906
1b	**2d**	80%	5.78781	5.72610	1.00000	5.68630	5.61910	0.43023	5.04724	4.98881	1.09490	4.90226	4.84274	0.25828
1b	**2e**	20%	5.94945	5.89352	1.00000	5.67549	5.60819	6.38128	5.20531	5.14369	1.19283	4.89722	4.82992	5.52503
1b	**2e**	35%	5.95619	5.90407	1.00000	5.67890	5.62000	2.63721	5.20926	5.15141	1.15928	4.90486	4.83710	2.30950
1b	**2e**	50%	5.96453	5.90407	1.00000	5.68776	5.62312	1.38972	5.22073	5.15975	1.13542	4.91164	4.84023	1.22419
1b	**2e**	65%	5.96818	5.90563	1.00000	5.69401	5.63146	0.79862	5.22073	5.16496	1.11002	4.91320	4.85378	0.70478
1b	**2e**	80%	5.97652	5.91397	1.00000	5.69922	5.64345	0.37035	5.22230	5.17174	1.04766	4.91998	4.86942	0.33594
1b	**2f**	20%	5.90324	5.85096	1.00000	5.69965	5.64598	4.78037	5.16291	5.11525	0.91679	4.91397	4.86261	4.36661
1b	**2f**	35%	5.90093	5.84864	1.00000	5.69734	5.64737	2.80549	5.16383	5.11386	0.91411	4.91628	4.86400	2.58834
1b	**2f**	50%	5.90232	5.84957	1.00000	5.69734	5.64459	1.52369	5.16522	5.11293	0.93093	4.91397	4.86261	1.40150
1b	**2f**	65%	5.90324	5.84864	1.00000	5.69734	5.64366	0.90245	5.16661	5.11016	0.94071	4.91489	4.86261	0.83780
1b	**2f**	80%	5.90093	5.85096	1.00000	5.69734	5.64737	0.51389	5.16383	5.11525	0.94566	4.91489	4.86631	0.48764
1c	**2a**	20%	5.08418	5.03451	1.00000	5.03451	4.99149	0.30380	4.91337	4.86817	0.91955	4.86817	4.82618	0.28617
1c	**2a**	35%	5.08258	5.03554	1.00000	5.03554	4.98908	0.48300	4.91337	4.86897	0.92136	4.86897	4.82010	0.45594
1c	**2a**	50%	5.08315	5.03898	1.00000	5.03164	4.98610	1.12534	4.91280	4.86943	0.91862	4.86473	4.82056	1.06820
1c	**2a**	65%	5.08372	5.03853	1.00000	5.02969	4.98059	1.76461	4.91337	4.86714	0.90675	4.86335	4.81815	1.66528
1c	**2a**	80%	5.08602	5.03956	1.00000	5.02763	4.97555	2.94200	4.91280	4.86679	0.89712	4.86335	4.81471	2.78473
1c	**2b**	20%	1.58603	1.55181	1.00000	1.50661	1.48886	0.92666	1.47366	1.45718	0.23981	1.41198	1.38199	0.20758
1c	**2b**	35%	1.58603	1.55307	1.00000	1.50238	1.48760	0.92593	1.46943	1.45042	0.46749	1.40944	1.37649	0.43442
1c	**2b**	50%	1.58180	1.54758	1.00000	1.50111	1.48760	0.90433	1.46816	1.45296	0.85182	1.40775	1.36973	0.79986
1c	**2b**	65%	1.58053	1.54758	1.00000	1.50238	1.48591	0.92814	1.46690	1.44746	1.40305	1.40226	1.37523	1.28570
1c	**2b**	80%	1.58349	1.54885	1.00000	1.50111	1.48337	0.92616	1.40522	1.36805	4.36330	1.46394	1.44493	1.12067
1c	**2c**	20%	5.22834	5.17948	1.00000	5.08665	5.06222	2.72160	5.03779	5.01581	0.79771	4.91565	4.86557	2.52494
1c	**2c**	35%	5.22650	5.17948	1.00000	5.08665	5.06222	2.21960	5.03779	5.01397	0.83271	4.91748	4.86923	2.09479

1c	**2c**	50%	5.22956	5.17337	1.00000	5.09092	5.06527	1.21734	5.03779	5.01581	0.84297	4.91870	4.86923	1.20189
1c	**2c**	65%	5.22650	5.17826	1.00000	5.08970	5.06527	0.70223	5.03657	5.01397	0.85976	4.91748	4.86740	0.70432
1c	**2c**	80%	5.22956	5.17948	1.00000	5.08970	5.06527	0.55731	5.03657	5.01397	0.84171	4.91870	4.87045	0.54912
1c	**2d**	20%	5.21260	5.15888	1.00000	5.08506	5.06235	3.36436	5.02261	4.99990	0.78818	4.91778	4.86537	3.31659
1c	**2d**	35%	5.21129	5.15888	1.00000	5.08768	5.06235	1.88916	5.02392	5.00164	0.79700	4.91778	4.86406	1.86463
1c	**2d**	50%	5.21129	5.16281	1.00000	5.09336	5.06672	0.88824	5.02697	4.99858	0.87226	4.92215	4.86537	0.94161
1c	**2d**	65%	5.21260	5.15582	1.00000	5.09205	5.06803	0.51003	5.02566	4.99422	0.83932	4.92652	4.86974	0.56308
1c	**2d**	80%	5.21522	5.15320	1.00000	5.09336	5.06803	0.28781	5.02566	5.00164	0.86457	4.92215	4.86843	0.33451
1c	**2e**	20%	5.35542	5.30475	1.00000	5.19687	5.14446	0.77647	5.08943	5.03702	3.11665	4.92084	4.86537	3.29236
1c	**2e**	35%	5.35848	5.30301	1.00000	5.19251	5.14446	0.74471	5.08943	5.02828	2.67407	4.92346	4.86275	2.92281
1c	**2e**	50%	5.35979	5.30301	1.00000	5.20255	5.14752	0.79634	5.09205	5.03964	1.39355	4.93045	4.86275	1.71665
1c	**2e**	65%	5.36110	5.30475	1.00000	5.20386	5.14315	0.83825	5.09205	5.04532	0.69679	4.92783	4.87673	1.02399
1c	**2e**	80%	5.36415	5.30738	1.00000	5.20386	5.15145	0.83466	5.09336	5.03527	0.37717	4.92652	4.87411	0.62804
1c	**2f**	20%	5.31792	5.26655	1.00000	5.16152	5.11664	0.60838	5.08332	5.03242	2.67452	4.91767	4.86261	2.77429
1c	**2f**	35%	5.31514	5.26285	1.00000	5.16522	5.11664	0.60769	5.08471	5.03103	2.09006	4.91489	4.86400	2.22306
1c	**2f**	50%	5.31792	5.26655	1.00000	5.16291	5.11293	0.64726	5.08332	5.03242	1.24448	4.91489	4.86631	1.43156
1c	**2f**	65%	5.31792	5.26655	1.00000	5.16383	5.11664	0.67053	5.08240	5.03705	0.63974	4.91397	4.86400	0.83854
1c	**2f**	80%	5.32023	5.26285	1.00000	5.16383	5.10923	0.71878	5.08332	5.03103	0.37385	4.91397	4.86400	0.56233
1d	**2a**	20%	1.93417	1.90072	1.00000	1.86885	1.84060	0.05150	1.50177	1.46719	0.75953	1.44459	1.40797	0.39579
1d	**2a**	35%	1.93327	1.89914	1.00000	1.86930	1.83788	0.09115	1.50064	1.46877	0.57742	1.44165	1.40594	0.62910
1d	**2a**	50%	1.93056	1.89756	1.00000	1.86297	1.83427	0.18977	1.49816	1.47081	0.29698	1.43532	1.40277	1.01812
1d	**2a**	65%	1.92423	1.89552	1.00000	1.86094	1.83269	0.32564	1.49544	1.46922	0.14306	1.43735	1.40390	1.34294
1d	**2a**	80%	1.92423	1.89552	1.00000	1.85778	1.82952	0.96134	1.49544	1.46922	0.02000	1.43464	1.39441	2.22214
1d	**2b**	20%	1.93834	1.89314	1.00000	1.85597	1.82851	0.01925	1.50534	1.46563	0.71514	1.41198	1.38072	0.25446

1d	**2b**	35%	1.93538	1.89990	1.00000	1.85047	1.82724	0.02874	1.50365	1.46563	0.57872	1.41325	1.37776	0.41197
1d	**2b**	50%	1.92863	1.89145	1.00000	1.85047	1.82175	0.05679	1.49689	1.46816	0.36172	1.41071	1.37100	0.66420
1d	**2b**	65%	1.93116	1.89441	1.00000	1.84794	1.82048	0.07774	1.49689	1.46690	0.26051	1.40944	1.37523	0.79954
1d	**2b**	80%	1.93116	1.89314	1.00000	1.84921	1.82048	0.09230	1.49562	1.46690	0.21896	1.40775	1.37227	0.89737
1d	**2c**	20%	1.99718	1.97288	1.00000	1.94087	1.90795	36.62300	1.54263	1.51834	10.30070	1.50336	1.47316	35.46260
1d	**2c**	35%	1.99559	1.97288	1.00000	1.93656	1.90454	21.12180	1.54263	1.51698	11.45400	1.50109	1.47361	15.36140
1d	**2c**	50%	1.99672	1.97107	1.00000	1.93361	1.90613	9.67968	1.54445	1.51471	9.15334	1.50109	1.47429	4.02437
1d	**2c**	65%	1.99491	1.97061	1.00000	1.93065	1.89841	6.90151	1.54263	1.51176	8.05233	1.49927	1.47429	1.69051
1d	**2c**	80%	1.99423	1.96880	1.00000	1.92816	1.90205	4.10123	1.54218	1.51176	5.96554	1.49677	1.47656	0.43780
1d	**2d**	20%	6.54547	6.51702	1.00000	6.46472	6.42707	9.62329	5.05464	5.02551	3.02434	4.88214	4.84809	6.89084
1d	**2d**	35%	6.54784	6.51661	1.00000	6.47494	6.43579	6.57211	5.05453	5.02513	3.48058	4.88887	4.85211	3.71559
1d	**2d**	50%	6.55186	6.51911	1.00000	6.48958	6.45683	2.40284	5.06745	5.02681	2.52758	4.89787	4.86448	0.76834
1d	**2d**	65%	6.55419	6.51549	1.00000	6.48869	6.45850	1.70488	5.02316	4.98627	2.23986	4.86266	4.82942	0.34472
1d	**2d**	80%	6.54672	6.51406	1.00000	6.47046	6.44406	0.76067	5.02108	4.98479	1.66135	4.86800	4.82799	0.05331
1d	**2e**	20%	6.71723	6.65589	1.00000	6.46905	6.41054	15.46000	5.21115	5.14603	4.31448	4.88936	4.82802	11.02180
1d	**2e**	35%	6.72572	6.66439	1.00000	6.48698	6.41998	7.09255	5.21964	5.15547	3.88226	4.90163	4.83746	4.11435
1d	**2e**	50%	6.72572	6.67099	1.00000	6.49358	6.42941	3.25571	5.22625	5.16208	2.94635	4.90163	4.84312	1.47916
1d	**2e**	65%	6.73233	6.67665	1.00000	6.51151	6.44168	1.67287	5.22625	5.16208	2.30669	4.91389	4.85539	0.57278
1d	**2e**	80%	6.73799	6.67382	1.00000	6.52661	6.45395	0.73700	5.23568	5.16491	1.74373	4.91672	4.86765	0.16174
1d	**2f**	20%	2.04376	2.01744	1.00000	1.93849	1.90363	9.32011	1.52877	1.50316	2.38652	1.50316	1.47424	7.91364
1d	**2f**	35%	2.04305	2.01815	1.00000	1.93374	1.90482	4.39544	1.52996	1.50388	2.30449	1.50316	1.47471	3.17308
1d	**2f**	50%	2.04376	2.01863	1.00000	1.93208	1.90553	2.64402	1.53043	1.50435	2.16084	1.50103	1.47661	1.56263
1d	**2f**	65%	2.04305	2.01697	1.00000	1.92876	1.90197	1.47365	1.52830	1.50269	1.89524	1.49984	1.47471	0.65320
1d	**2f**	80%	2.04423	2.01863	1.00000	1.92639	1.89865	1.79275	1.52830	1.50388	1.98795	1.50150	1.47756	0.93996

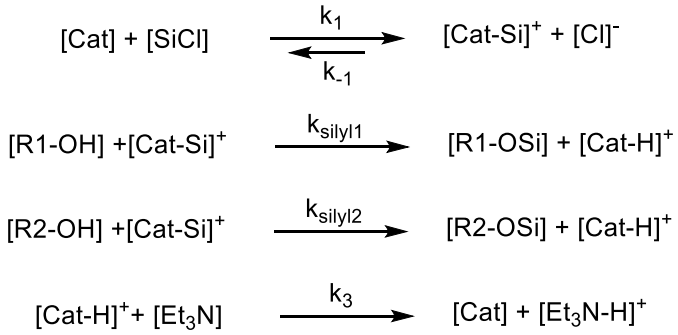
1e	**2a**	20%	1.62039	1.58725	1.00000	1.55165	1.52997	0.26578	1.50297	1.47249	1.17088	1.44139	1.41521	0.32362
1e	**2a**	35%	1.62223	1.58725	1.00000	1.54940	1.52240	0.48552	1.50338	1.47494	1.15752	1.43853	1.41194	0.58139
1e	**2a**	50%	1.61568	1.58868	1.00000	1.54654	1.51811	1.79556	1.49826	1.47453	1.14615	1.43321	1.40662	2.15616
1e	**2a**	65%	1.61609	1.58766	1.00000	1.54654	1.52097	0.95769	1.50051	1.47249	1.17447	1.43751	1.40478	1.17450
1e	**2a**	80%	1.61241	1.58623	1.00000	1.54224	1.51565	3.75866	1.49867	1.47065	1.16511	1.43710	1.40109	4.66188
1e	**2b**	20%	1.62151	1.58729	1.00000	1.52308	1.50365	0.18471	1.50365	1.46943	1.24818	1.41325	1.38579	0.22702
1e	**2b**	35%	1.62320	1.58603	1.00000	1.52731	1.50111	0.40105	1.50111	1.47112	1.23497	1.41198	1.38072	0.48026
1e	**2b**	50%	1.62320	1.58898	1.00000	1.53111	1.49985	0.69398	1.49985	1.46943	1.26615	1.41494	1.37100	0.87864
1e	**2b**	65%	1.62151	1.58476	1.00000	1.52562	1.49689	1.22429	1.49689	1.46690	1.26066	1.41494	1.37354	1.55677
1e	**2b**	80%	1.61348	1.58349	1.00000	1.52308	1.49436	1.98789	1.49436	1.46267	1.36217	1.40522	1.37354	2.64594
1e	**2c**	20%	5.24682	5.20292	1.00000	5.10327	5.05850	6.35680	5.05764	5.01806	1.05479	4.91322	4.86267	7.71065
1e	**2c**	35%	5.24942	5.20292	1.00000	5.10587	5.06023	5.17535	5.06023	5.01720	0.99901	4.91408	4.86614	6.26842
1e	**2c**	50%	5.24856	5.20292	1.00000	5.10587	5.06110	2.69189	5.06110	5.01720	1.03212	4.91322	4.86845	3.27953
1e	**2c**	65%	5.24769	5.20292	1.00000	5.10674	5.06197	1.72921	5.06197	5.01720	1.04347	4.91495	4.86845	2.18195
1e	**2c**	80%	5.24682	5.19945	1.00000	5.10847	5.06283	1.02203	5.06197	5.01373	1.05914	4.91582	4.86758	1.30702
1e	**2d**	20%	5.23793	5.18290	1.00000	5.11476	5.05536	2.25076	5.04969	5.00426	0.81412	4.91778	4.86275	2.41247
1e	**2d**	35%	5.24099	5.18552	1.00000	5.10909	5.05536	1.74104	5.04838	4.99596	0.82590	4.91647	4.86406	1.91619
1e	**2d**	50%	5.23924	5.18552	1.00000	5.11782	5.05973	0.90549	5.05231	4.99858	0.87470	4.92346	4.86406	1.05072
1e	**2d**	65%	5.24230	5.17853	1.00000	5.12044	5.06235	0.52537	5.05231	4.99990	0.90145	4.92783	4.86974	0.65173
1e	**2d**	80%	5.24667	5.17722	1.00000	5.12350	5.06366	0.26578	5.05536	4.99727	0.93756	4.92477	4.87105	0.36138
1e	**2e**	20%	5.38250	5.32310	1.00000	5.19687	5.14184	0.76191	5.10909	5.05100	4.80203	4.92783	4.85838	5.46271
1e	**2e**	35%	5.37988	5.32747	1.00000	5.19993	5.15014	0.74130	5.11040	5.05667	2.49705	4.92477	4.86843	3.06359
1e	**2e**	50%	5.38818	5.33140	1.00000	5.19993	5.15014	0.78588	5.11476	5.05667	1.20303	4.92652	4.87105	1.75583
1e	**2e**	65%	5.38687	5.32878	1.00000	5.20823	5.15320	0.83966	5.11607	5.06235	0.66574	4.93351	4.86974	1.15825

1e	**2e**	80%	5.39123	5.32878	1.00000	5.20692	5.15451	0.84816	5.11607	5.06672	0.36483	4.92477	4.87804	0.69825
1e	**2f**	20%	5.33126	5.30363	2.00000	5.16321	5.11921	1.01766	5.10156	5.05475	5.71865	4.91356	4.86675	8.39753
1e	**2f**	35%	5.32563	5.30312	2.00000	5.16039	5.11716	1.12948	5.10079	5.05757	2.40740	4.91228	4.86675	4.17076
1e	**2f**	50%	5.32512	5.30235	2.00000	5.16039	5.11793	1.28935	5.10233	5.05833	1.03432	4.91356	4.86752	2.33393
1e	**2f**	65%	5.32559	5.30245	2.00000	5.15962	5.11636	1.59191	5.10102	5.05852	0.45295	4.91191	4.86942	1.40133
1e	**2f**	80%	5.32308	5.30219	2.00000	5.15940	5.11641	1.85906	5.10014	5.05716	0.19720	4.91363	4.87065	0.85028
1f	**2a**	20%	1.77688	1.74886	1.00000	1.70528	1.67685	0.22854	1.50379	1.47310	0.86126	1.44221	1.41296	0.32458
1f	**2a**	35%	1.77688	1.74783	1.00000	1.70344	1.67787	0.35938	1.50583	1.46921	0.80755	1.44282	1.41091	0.50011
1f	**2a**	50%	1.77913	1.74599	1.00000	1.70242	1.67010	0.65828	1.50154	1.47065	0.71967	1.43935	1.40662	0.86218
1f	**2a**	65%	1.77729	1.74599	1.00000	1.69915	1.66785	1.17562	1.50297	1.47024	0.62305	1.43566	1.40437	1.47037
1f	**2a**	80%	1.77586	1.74845	1.00000	1.70099	1.66171	2.35313	1.50051	1.46880	0.50173	1.43505	1.40396	2.77359
1f	**2b**	20%	1.74308	1.70838	1.00000	1.68015	1.65578	0.22236	1.48118	1.44979	0.88260	1.40531	1.38094	0.31036
1f	**2b**	35%	1.74127	1.70724	1.00000	1.67637	1.64788	0.35895	1.47483	1.44938	0.82273	1.40256	1.37512	0.49129
1f	**2b**	50%	1.73894	1.70393	1.00000	1.67067	1.63916	0.60632	1.47576	1.44075	0.76232	1.39669	1.36780	0.80669
1f	**2b**	65%	1.73194	1.70345	1.00000	1.66094	1.62599	1.27058	1.46842	1.43961	0.65012	1.38593	1.35602	1.62790
1f	**2b**	80%	1.72574	1.69792	1.00000	1.64976	1.61775	2.06947	1.45974	1.43321	0.51574	1.37395	1.34570	2.49620
1f	**2c**	20%	6.11388	6.06380	1.00000	6.00945	5.95632	7.50888	5.06527	5.01581	1.25821	4.91381	4.86251	6.73365
1f	**2c**	35%	6.11205	6.05770	1.00000	6.01250	5.95937	3.09226	5.06405	5.01397	1.26528	4.91565	4.86740	2.67282
1f	**2c**	50%	6.11083	6.06075	1.00000	6.00578	5.95632	1.81124	5.06222	5.01397	1.23446	4.91381	4.86251	1.46341
1f	**2c**	65%	6.11083	6.05770	1.00000	6.01861	5.96425	0.99604	5.06405	5.01214	1.21130	4.92053	4.86557	0.75300
1f	**2c**	80%	6.10900	6.05892	1.00000	6.01250	5.96425	0.75354	5.06405	5.01214	1.16041	4.91565	4.86251	0.51799
1f	**2d**	20%	6.12175	6.05498	1.00000	5.96317	5.88903	4.26777	5.06175	5.00382	1.07247	4.89040	4.82461	3.84770
1f	**2d**	35%	6.12151	6.04909	1.00000	5.97305	5.89656	2.25835	5.06420	4.99812	1.08746	4.90035	4.82929	1.99989
1f	**2d**	50%	6.12123	6.04212	1.00000	5.97687	5.90084	1.19653	5.07113	4.98945	1.04504	4.90571	4.82813	1.01111

1f	**2d**	65%	6.11932	6.05050	1.00000	5.98024	5.91676	0.63325	5.06437	4.99555	1.04704	4.90106	4.83613	0.51472
1f	**2d**	80%	6.11378	6.04916	1.00000	5.99149	5.92091	0.36016	5.05846	4.99633	1.01702	4.90934	4.83726	0.26317
1f	**2e**	20%	6.27832	6.21263	1.00000	5.97363	5.90001	4.37817	5.22380	5.15810	0.80789	4.90438	4.83868	4.03301
1f	**2e**	35%	6.28625	6.21602	1.00000	5.97703	5.90793	2.25553	5.23172	5.15810	0.79673	4.91910	4.84208	2.20881
1f	**2e**	50%	6.29305	6.21263	1.00000	5.99175	5.91473	1.07624	5.22833	5.16150	0.81270	4.91910	4.84888	1.11442
1f	**2e**	65%	6.29758	6.21602	1.00000	5.99968	5.92266	0.58623	5.23512	5.16150	0.86972	4.91910	4.86021	0.68025
1f	**2e**	80%	6.29758	6.22395	1.00000	5.99968	5.93738	0.28827	5.23512	5.17962	0.90014	4.93383	4.85681	0.40021
1f	**2f**	20%	6.20725	6.15218	1.00000	6.00226	5.95090	3.66391	5.16661	5.11664	0.35463	4.91767	4.86122	4.01925
1f	**2f**	35%	6.20493	6.14848	1.00000	6.00967	5.95368	1.66815	5.16661	5.11895	0.39781	4.91628	4.86261	2.10737
1f	**2f**	50%	6.20586	6.14987	1.00000	6.00967	5.95461	0.83239	5.16661	5.11525	0.43365	4.91767	4.86631	1.29326
1f	**2f**	65%	6.20216	6.14756	1.00000	6.00597	5.95229	0.44139	5.16892	5.11664	0.49106	4.91628	4.86122	0.88055
1f	**2f**	80%	6.20216	6.14848	1.00000	6.00597	5.95368	0.17562	5.16522	5.11756	0.62702	4.91628	4.86400	0.50351

2.4. Simulation of Competition Experiments

Competition experiments were simulated using CoPaSi[2] according to Scheme S3.



Scheme S3: Model reaction for the simulation of Selectivity curves

Presuming that the reaction between the alcohol and the loaded catalyst is the rate limiting step, the values of k_1, k_{-1} and k_3 were fixed for all the simulations to:

$k_1 = 0.1 \frac{l}{mol\, s}$; $k_{-1} = 0.001 \frac{l}{mol\, s}$; $k_3 = 0.1 \frac{l}{mol\, s}$.

Setting arbitrarily $k_{silyl1} = 0.01 \frac{l}{mol\, s}$, k_{silyl2} can be calculated using the relative rate constant received from Eq. S6 by:

$$k_{silyl2} = k_{rel} \cdot k_{silyl1} = k_{rel} \cdot 0.01 \frac{l}{mol \cdot s} \qquad \text{Eq. S7}$$

From those rate constants and the experimental starting concentrations the concentrations of all relevant species along the reaction path were calculated by CoPaSi. The resulting time and concentration values were used to calculate the chemoselectivity by Eq. S3 and the conversion by Eq. S2. Plotting those values using ProFit[3] allowed us to compare experimental results with the simulation and to verify the calculated relative rate constants as shown in in Figure S4 to Figure S8.

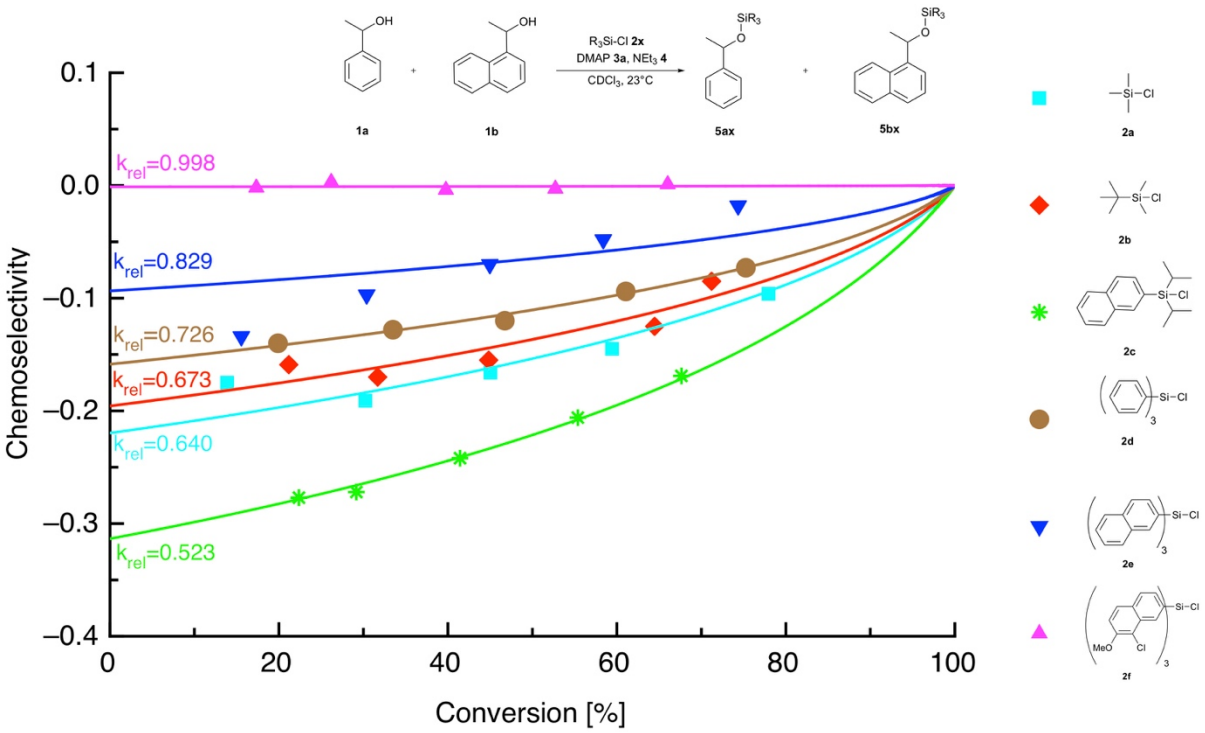


Figure S4: Plot of conversion vs. chemoselectivity values for competition experiments of alcohol **1a** and **1b**. The curves for the average relative rate constant were simulated using CoPaSi (see Chapter 2.4).

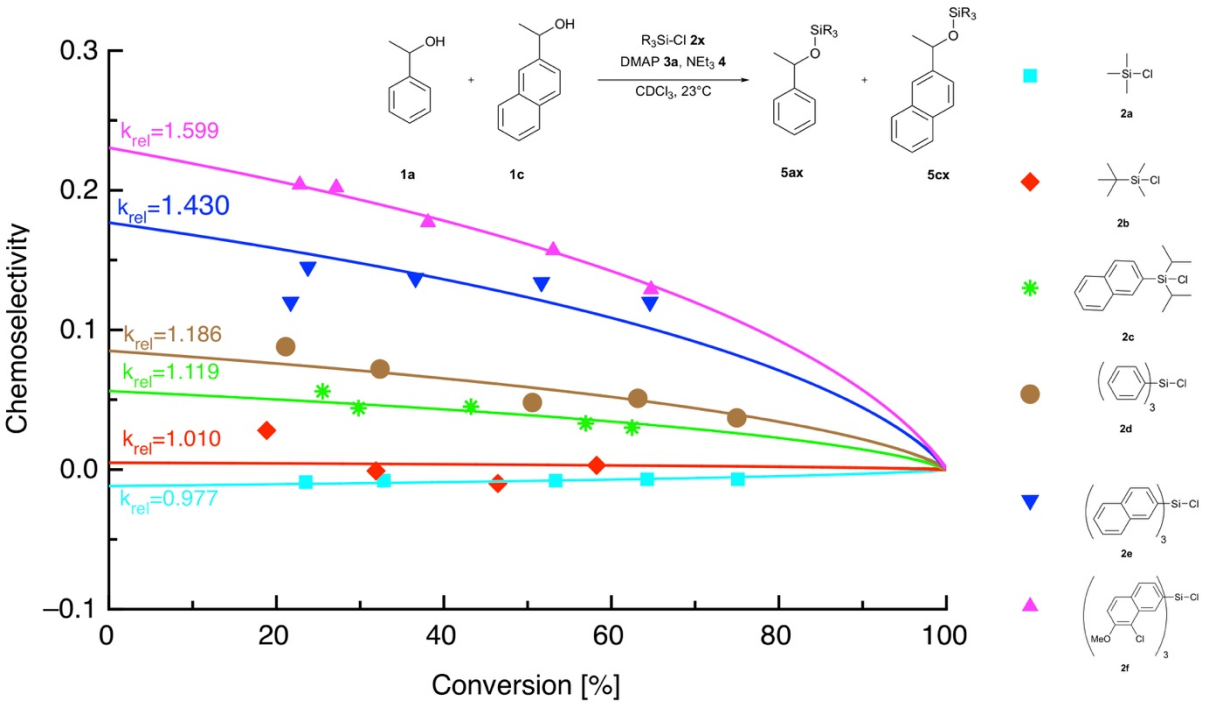


Figure S5: Plot of conversion vs. chemoselectivity values for competition experiments of alcohol **1a** and **1c**. The curves for the average relative rate constant were simulated using CoPaSi (see Chapter 2.4).

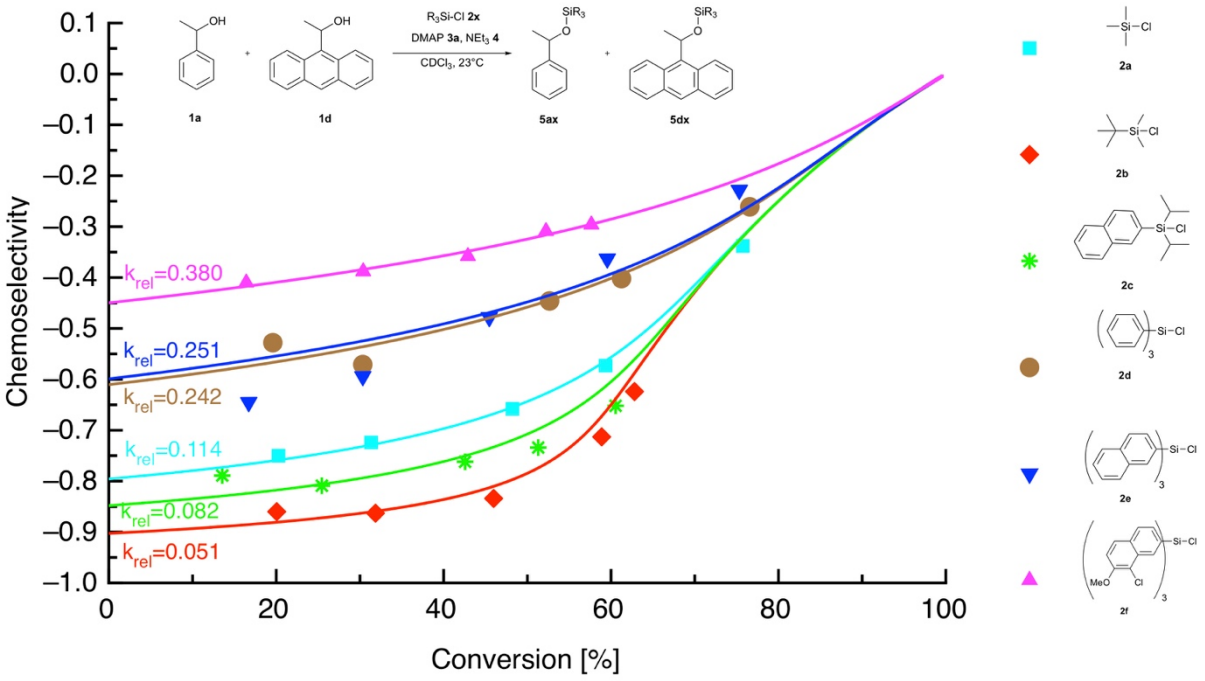


Figure S6: Plot of conversion vs. chemoselectivity values for competition experiments of alcohol **1a** and **1d**. The curves for the average relative rate constant were simulated using CoPaSi (see Chapter 2.4).

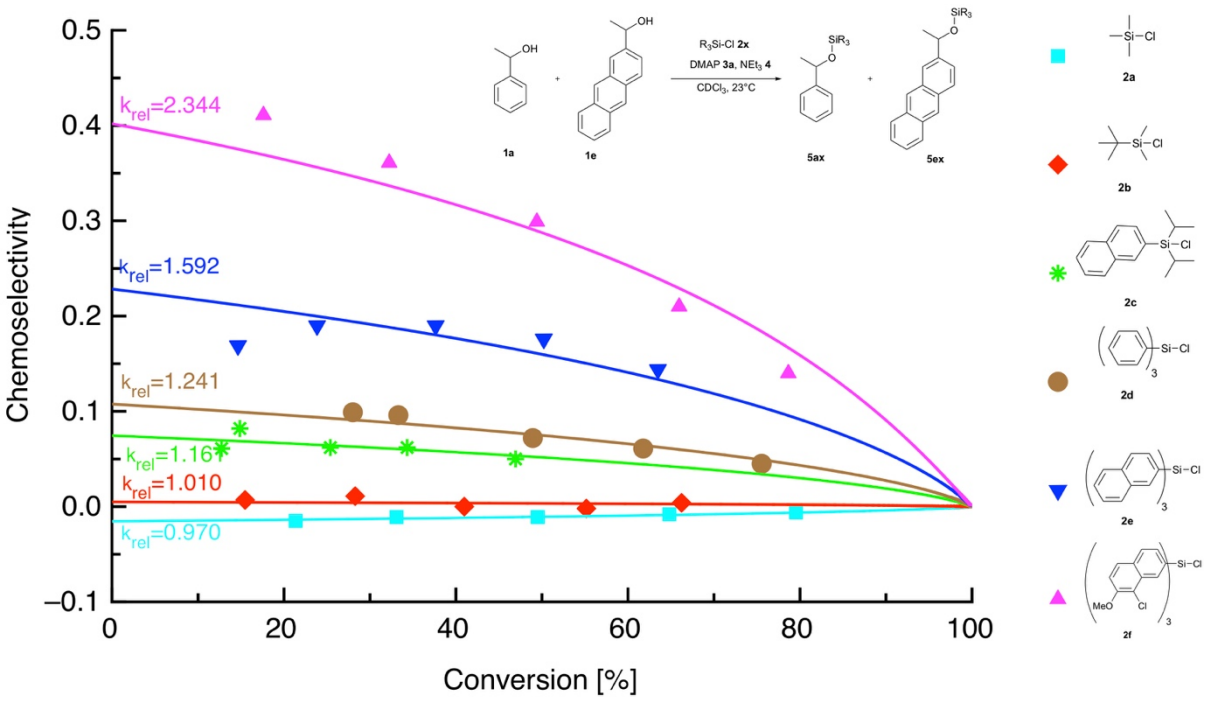


Figure S7: Plot of conversion vs. chemoselectivity values for competition experiments of alcohol **1a** and **1e**. The curves for the average relative rate constant were simulated using CoPaSi (see Chapter 2.4).

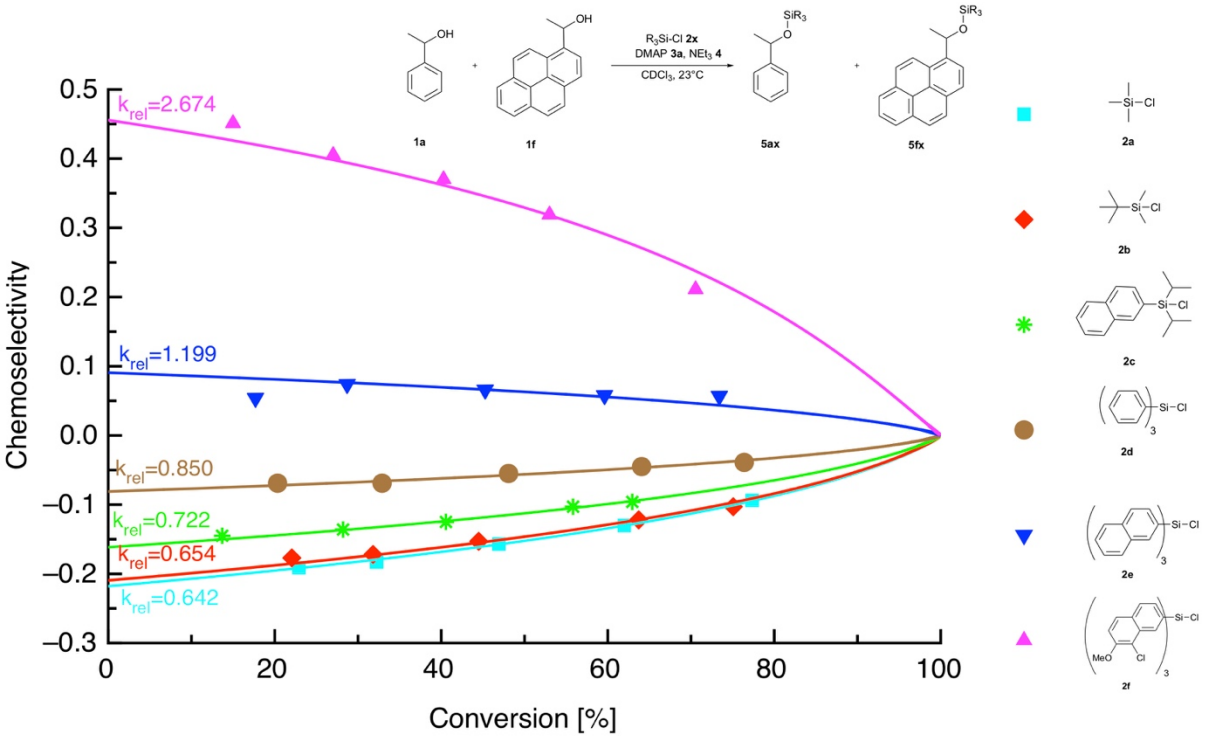
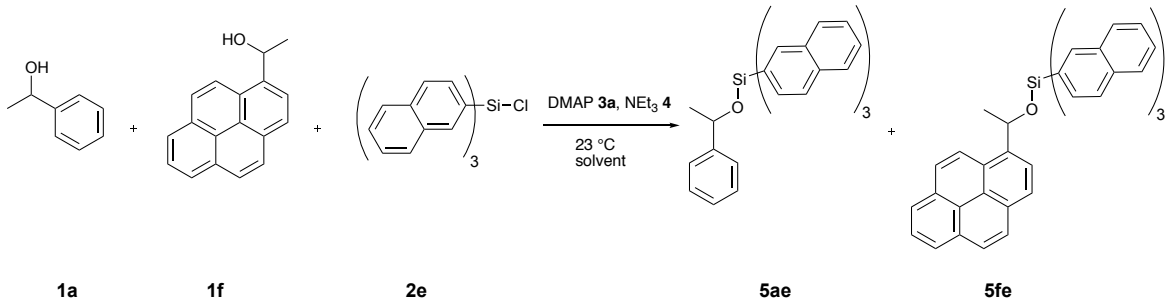


Figure S8: Plot of conversion vs. chemoselectivity values for competition experiments of alcohol **1a** and **1f**. The curves for the average relative rate constant were simulated using CoPaSi (see Chapter 2.4).

3. Investigation of Solvent Effects

3.1. Methodology of Solvent Competition Experiments

The influence of various solvents on the relative rate constant and therewith on dispersion forces was investigated. As a benchmark reaction, the competition experiment between alcohol **1a** and **1f** and silyl chlorid **2e** was used (Scheme S4). Reason for the choice of this reaction were, that 1) we were able to observe small influences of the solvent as rate constants of both alcohol are quite similar (k_{rel} = 1.199 in $CDCl_3$); 2) alcohol **1e** shows as well attractive dispersive forces as repulsive steric effects, so it is possible to examine the whole scope of solvent effects.



Scheme S4: Benchmark reaction used for solvent screening.

The competition experiments were proceeded as similar as possible to the method described in chapter 2.1. Instead of measuring five different conversions, the experiment with 50% of silyl chloride relative to both alcohols was repeated three times. All solvents were purchased "extra dry" or were dried following typical procedures (see chapter 5.1).[4] To be able to measure ^{1}H-NMR spectra after full conversion, different methods had to be applied:

Method A: As far as possible and reasonable the experiments were done in deuterated solvents (DMSO, Acetone, DCM). With 0.6 mL of the reaction mixture a ^{1}H-NMR spectrum was measured, using the corresponding solvent residual signal as reference.

Method B: If hydrogen-atom-free solvents (CS_2, C_6F_6, CCl_4) were used, after full conversion 0.3 mL of the reaction mixture and 0.3 mL of $CDCl_3$ were mixed in the NMR-tube and a ^{1}H-NMR spectrum using the $CDCl_3$-signal as a reference was recorded.

Method C: In all other cases after full conversion the solvent was removed under reduced pressure using a cannula through the septum of the GC-vial. Then the vial was purged with N_2 and 1.5 mL of $CDCl_3$ were added in order to resolve the reaction

mixture. 0.6 mL of this solution were transferred to a NMR-tube and a ^{1}H-NMR using the $CDCl_3$-signal as a reference was recorded.

To ensure that all methods lead to the same result, some experiments were carried out using different methods as well as different amounts of silyl chloride. As Table S9 shows, the results are reproducible among the different conditions.

Table S9: Relative rate constants in different solvents measured using different methods.

Solvent	Method	Amount of silyl chloride	Relative rate constant
DCM	A	20%	1.354±0.025
	C	50%	1.379±0.036
CCl_4	B	50%	0.836±0.047
	C	50%	0.868

A wide range of other solvents could not to be used due to bad solubility or unwanted side reactions (compare Table S10).

Table S10: Not suitable solvents for competition experiments of the benchmark reaction following Scheme S4.

Solvents	Problem
Hexafluoropropanol, Acetonitrile (pure), *tert*-Amylalcohol (pure), Diethyl ether, Triethylamine, Methyl *tert*-Butyl Ether, *N,N*-Diisopropylethylamine	silyl chloride **2e** and **2f** not soluble
Hexafluorobenzene (pure)	Alcohol **1f** not soluble
Dichloromethyl methyl ether	Side reaction with NEt_3 and alcohols

If a possibly reactive solvent (acetone, DMSO, *tert*-amylalcohol[5]) was used, a blind probe was performed. Therefore, silyl chloride **2e**, DMAP **3a** and triethylamine **4** were solved in the corresponding solvent. A ^{1}H-NMR spectrum was recorded to ensure, that no background reaction with the solvent did happen. In the case of DMSO a non-specified background reaction between solvent and silyl chloride occurred in the blind probe, which led to the precipitation of NEt_3HCl. This led to a lower conversion rate than expected in the competition experiments.

3.2. Results of Solvent Experiments

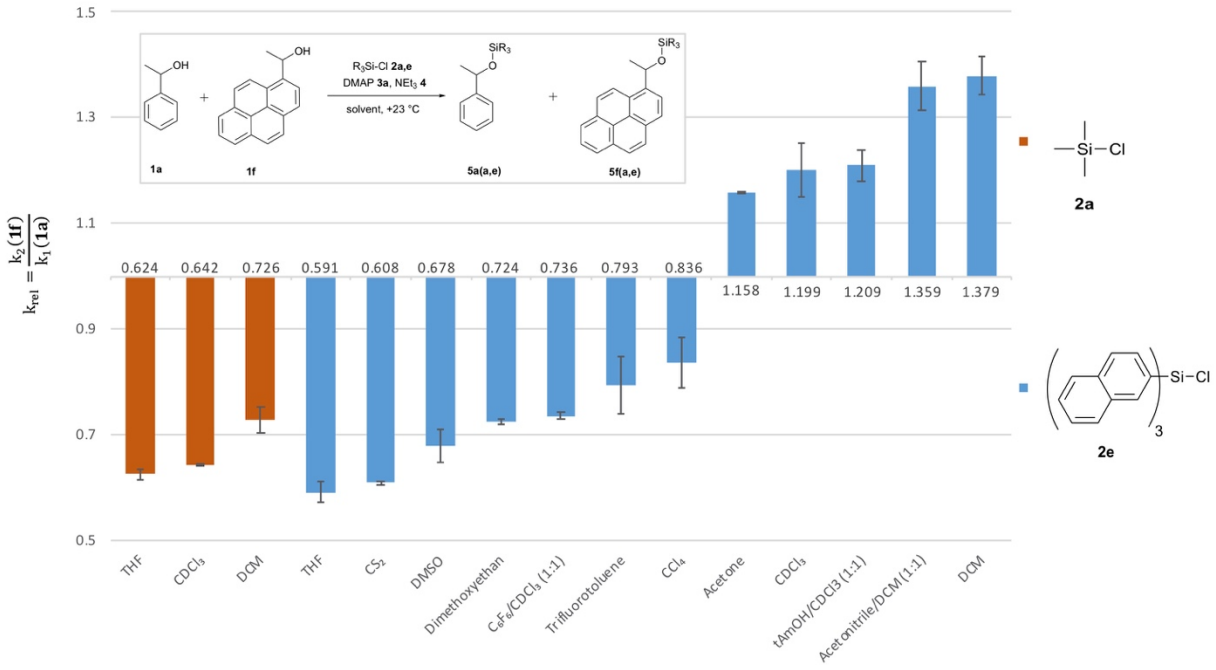


Figure S9: Relative rate constants of competition experiment between alcohol **1a** and **1f** with silyl chloride **2a** or **2e** in various solvents.

The results in Figure S9 show the big influence of the solvents on the relative rate constants, as long as the DED **2e** is used as silylation agent. In the case of non-aromatic TMS **2a** the effect of solvents is minor.

Interestingly the relative rate constant with **2e** approach those of the "size-effect-free" reaction with TMS **2a** for several solvents. This allows to state that for those solvents size effects plays only a minor role in the formation of the silyl ethers, even if the reactants bear two big surfaces.

To prove that the differences in rate constants are due to the influence of the solvent on size effects, competition experiments with different systems were carried out in the three solvents THF, $CDCl_3$ and DCM (Figure S10).

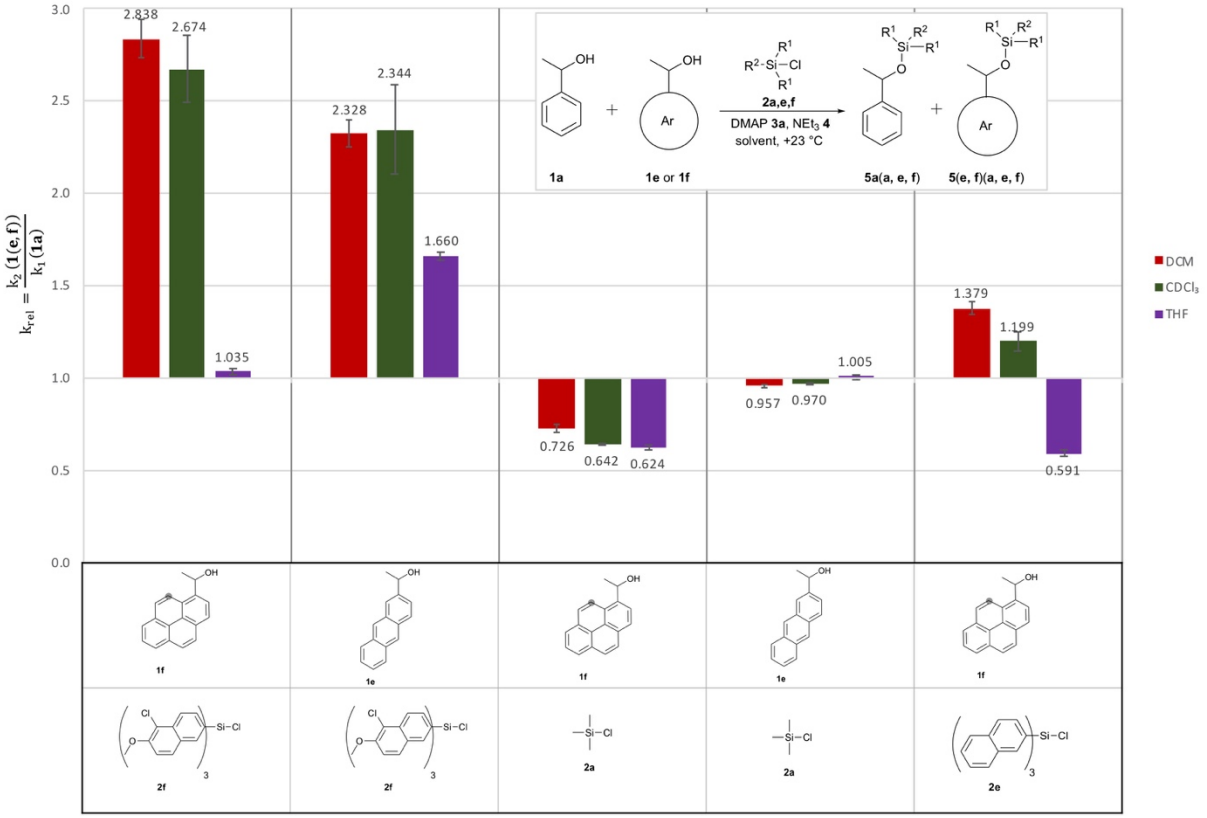


Figure S10: Relative rate constants in DCM, $CDCl_3$ and THF for various alcohols and silyl chlorides.

In those results the following trends can be observed:

1. The observed solvent effects are caused by size effects. If systems without a high degree of aromatic overlapping like those with TMS **2a** are investigated, solvent effects are minor.
2. THF seems to lower size effects dramatically compared to $CDCl_3$ and DCM. Therefore, the influence on dispersive interaction seems to be a solvent property.
3. The rate constants for the investigated alcohol only vary between DCM and $CDCl_3$ if alcohol **1f** is used. The main difference between **1f** and **1a** is the possibility of 1,5-interactions between the *peri* hydrogen atoms and the hydroxyl reactive site in the case of alcohol **1f**. It is likely that DCM lowers those interactions, while $CDCl_3$ and THF do not influence on them. This could also explain why alcohol **1f** reacts a little faster with TMS **2e** in DCM than in $CDCl_3$ and THF.

3.3. Short Overview of Selected Solvent Parameters

In order to find an explanation for the differences in rate constants due to different solvents, herein a short overview of the different used solvent parameters is given.

Kamlet-Taft developed the linear solvation energy relationship which allows to distinguish the different contributions of hydrogen-bond donor (α), hydrogen-bond acceptor (β), polarizability (π^* and δ) to solvation.[6]

Abraham refined this scale naming the new hydrogen-bond basicity and acidity parameters β_2^H and α_2^H.[7, 8]

One of the major limitations of the Kamlet-Taft-model is, that all less polar hydrogen-bond donor than CCl_4 were assigned due to the experimental determination with α=0 leading to an error for non-polar solvents. Interpretating all intermolecular interactions except aromatic stacking as interactions between electron-rich and electron-poor regions of a molecule and therewith as a form of hydrogen bonds, Hunter redefined α and β referring them to the maximal and minimal energy of the molecules electrostatic potential surface.[9]

The energy that is needed to break the intermolecular forces between solvent molecules in order to bring them to gas phase can be described by the internal energy of vaporization $\Delta_{vap}U°$. Through norming this value by division through the molar volume of the solvent as shown in Eq. S8 the cohesive energy density (*ced*) can be calculated.[10-12]

$$ced = \frac{\Delta_{vap}U°}{V_m} \qquad \text{Eq. S8}$$

The Hildebrand parameter δ_H is closely related to the *ced* by Eq. S9.[12]

$$\delta_H = \sqrt{ced} = \left(\frac{\Delta_{vap}U°}{V_m}\right)^{\frac{1}{2}} \qquad \text{Eq. S9}$$

Therefore, *ced* and δ_H are indicators for the strength of the intermolecular forces between solvent molecules.

Hansen expanded Hildebrand's understanding of solubility taking into account the three different forces that influence on the solubility of a compound. Those are non-polar, dispersive forces (δ_d), polar-polar forces (δ_p) and hydrogen bonds (δ_h).[13, 14]

$$\delta_H^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \text{Eq. S10}$$

The three Hansen parameters can be measured experimentally. The compound is solved in a solvent in which it is good soluble. Solvents in which the compound is insoluble are added to determine the mixture at which phase separation takes place. Putting those number in a three-dimensional sphere gives the numbers of interest.[14]

The solvent parameter $E_T\ (30)$ uses the solvatochromism of Reichardt's dye 30 to describe the polarity of a solvent. The stronger the polar interactions between the polar dye and the solvent molecules are, the shorter the wavelength of the absorbed light has to be. The $E_T\ (30)$ is gained by measuring an UV/vis-spectrum of the solved dye and putting the resulting maximum of absorption in Eq. S11.[15, 16]

$$E_T\ (30) = hcN_A\tilde{\nu}_{max} \qquad \text{Eq. S11}$$

The $E_T\ (30)$ value is an indicator for the polarity of a solvent.

Similarly, for Catalán's polarity-polarizability scale (SPP) the UV/vis-spectrum of 2-(Dimethylamino)-7-nitrofluorene (DMANF) is investigated. As the solvation of DMANF is driven as well by van der Waals forces as polar intermolecular interactions, this scale measures both polar and nonpolar solvent properties.[17]

In contrast for the solvent polarizability scale (SP) a nonpolar dye is used, so that only dispersive interactions are involved in the solvation process and only those interactions will determine the maximum absorption. As dispersive interactions are a function of the polarizability of both compounds, those values can be used to set up a relative scale of polarizabilities of solvents.[18]

Presuming that SPP is measuring nonpolar and polar interactions, whereas SP measures only the nonpolar part, it is possible compare those scales, in order to get a scale of the polar interactions. Polar interactions are caused by the permanent dipole moment of a molecule, which allows to derive the solvent dipolarity scale (SdP).[19]

3.4. Tables of relative rates and relevant solvent parameters

Table S11: Relative rate constant for the competition experiment of alcohol **1a** and **1f** with silyl chloride **2e**, Hunter parameter and Kamlet-Taft parameters. Those parameters were used to fit parameters and predict ln k_{rel}. [a]Calculated from α_2^H by $\alpha = 4.1(\alpha_2^H + 0.33)$.[9] [b]Geometry of solvents was optimized at B3LYP/6-31G(d) level of theory, maxima and minima of the electrostatic potential surface were calculated by using Multiwfn 3.6 program[25] over the isodensity surface with a radius=0.002 Bohr Å^{-3}.[20] [c]Calculated from β_2^H by $\beta = 10.3(\beta_2^H + 0.06)$.[9]

	k_{rel}	ln(k_{rel})	StDev ln(k_{rel})	α^{20}	β^{20}	*ln (k_{rel}) predicted*	π^{*21}	β^{21}	α^{21}	δ^{21}	*ln (k_{rel}) predicted*
				Hunter hydrogen-bond donor	*Hunter hydrogen-bond acceptor*	*- 1.13 + 0.66 α + 0.032 β*	*Kamlet-Taft polarization parameter*	*Kamlet-Taft hydrogen-bond acceptor parameter*	*Kamlet-Taft hydrogen-bond donor parameter*	*Kamlet-Taft polarizability correction factor*	-0.34 -0.24 π* +0.26 β +3.67 α +0.27 δ
THF	**0.591**±0.018	-0.526	0.031	*0.8*[b]	5.9	-0.42	0.55	0.55	0.00	0.00	-0.33
CS_2	**0.608**±0.004	-0.498	0.007	*0.9*[b]	1.3[22,c]	-0.47	0.51	0.07	0.00	0.00	-0.44
Dimethoxy-ethan	**0.724**±0.006	-0.322	0.008	*0.8*[b]	5.3	-0.43	0.53[6]	0.41[6]	0.00[6]	0.00[6]	-0.36
Trifluorotoluene	**0.793**±0.055	-0.232	0.069	*1.3*[b]	*1.7*[b]	-0.25	0.64[23]	0.00[23]	0.00[23]	1.00[23]	-0.22
CCl_4	**0.836**±0.047	-0.179	0.056	*1.4*	*0.6*	-0.19	0.21	0.10	0.00	0.50	-0.23
Acetone	**1.158**±0.002	0.147	0.002	1.5[24,a]	5.7[24,c]	0.04	0.62	0.48	0.08	0.00	-0.07
$CDCl_3$	**1.199**±0.051	0.182	0.051	2.2	0.8	0.34	0.69	0.10	0.20	0.50	0.39
DCM	**1.379**±0.036	0.321	0.027	1.9	2.0	0.18	0.73	0.10	0.13	0.50	0.13
DMSO	**0.678**±0.031	-0.389	0.045	*0.8*[9]	8.9	-0.32	1.00	0.76	0.00	0.00	-0.38

Table S12: Compilation of relative rate constants and solvent parameters. Solvent mixtures are reported in v/v. For deuterated solvents the value of the non-deuterated solvents are given. [a]Relative rate constants and standard deviations of the competition experiment shown in Scheme S4. [b]ced values were calculated from the Hildebrand solubility parameters by ced=δ_H^2. [c]For solvent mixtures a linear relationship between the parameters of pure solvents depending on the v/v%-composition was assumed. As only 1:1-mixtures were used, the given values were calculated as the average of the values of the corresponding solvent. [d]In the case of DMSO a non-specified background reaction between solvent and silyl chloride occurred in the blind probe, which led to the precipitation of NEt_3HCl.

	$k_{rel} = \frac{k(1f)}{k(1a)}$ [a]	***ced*** [12, 26] [cal/cm^3][b] *Intermolecular forces of solvent molecules*	$E_T(30)$ [16] [kcal/mol] *polarity*	**SP** [18, 19] *Solvent Polarizability*	**SdP** [19] *Solvent Dipolarity*	δ_d [27] *Hansen dispersion parameter*	δ_p [27] *Hansen polar parameter*	δ_h [27] *Hansen Hydrogen-bond parameter*
THF	**0.591**±0.018	86.3	37.4	0.7139	0.634	16.8	5.7	8.0
CS_2	**0.608**±0.004	99.5	32.8	1.000	0	20.2	0	0.6
DMSO[d]	**0.678**±0.031	169.2	45.1	0.829	1.000	18.4	16.4	10.2
Dimethoxyethan	**0.724**±0.006	78.3	38.2	0.680	0.625	15.4	6.3	6
C_6F_6/$CDCl_3$ (1:1)	**0.736**±0.008	77.5[c]	36.7[c]	0.7031[c]	0.433[c]	15.8[c]	5.2[c]	3.5[c]
Trifluorotoluene	**0.793**±0.055	68.3	38.7	0.6938	0.663	17.5	8.8	0
CCl_4	**0.836**±0.047	74.1	32.4	0.7677	0	17.8	0	0.6
Acetone	**1.158**±0.002	92.8	42.3	0.6510	0.907	15.5	10.4	7.0
$CDCl_3$	**1.199**±0.051	85.4	39.0	0.7833	0.614	17.8	3.1	5.7
tAmOH/CDCl3 (1:1)	**1.209**±0.03	97.7c	40.2[c]	n.a.	n.a	16.7c	4.7c	9.5[c]
AcCN/DCM (1:1)	**1.359**±0.046	118.9[c]	43.15[c]	0.7030[c]	0.872[c]	16.2[c]	12.5[c]	6.7c
DCM	**1.379**±0.036	98.5	40.7	0.7612	0.769	17	7.3	7.1

3.5. Discussion of the Influence of Solvent Properties on the Rate Constant

In order to analysis the influence of solvent properties on the relative rate constant a linear solvation energy relationship was performed, as recent research proved it a suitable way for rationalizing solvent effects in noncovalent interactions.[28] Analysis of experimental k_{rel} with literature parameters (Table S11) and fitting the parameters for hydrogen-bond donor (α), hydrogen-bond acceptor (β) and polarizability (π^* and δ) with StatPlus[29] led to Eq. S12.

$$k_{rel} = -0.34 - 0.24\,\pi^* + 0.26\,\beta + 3.67\,\alpha + 0.27\,\delta \qquad \text{Eq. S12}$$

Eq. S12 strikingly proves, that solvent effects are widely independently of the polarizability of the solvent but correlate strongly with the hydrogen bond donor ability of the solvent.

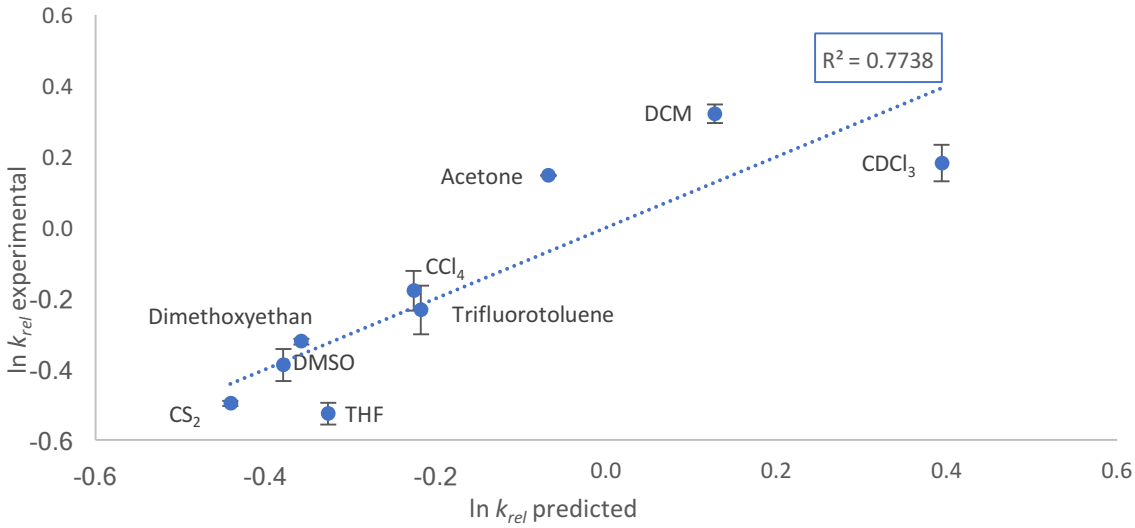


Figure S11: Kamlet-Taft-Plot of predicted ln k_{rel} values using Eq. S12 against experimental ln k_{rel} values.

The plot of predicted and experimental values in Figure S11 gives a moderate correlation. One of the major limitations of the Kamlet-Taft-model is, that all less polar hydrogen-bond donor than CCl_4 were assigned due to the experimental determination with α=0 leading to an error for non-polar solvents. Indeed, using Hunter's α and β values and fitting parameters led to Eq. S13.

$$k_{rel} = -1.13 + 0.66\,\alpha + 0.032\,\beta \qquad \text{Eq. S13}$$

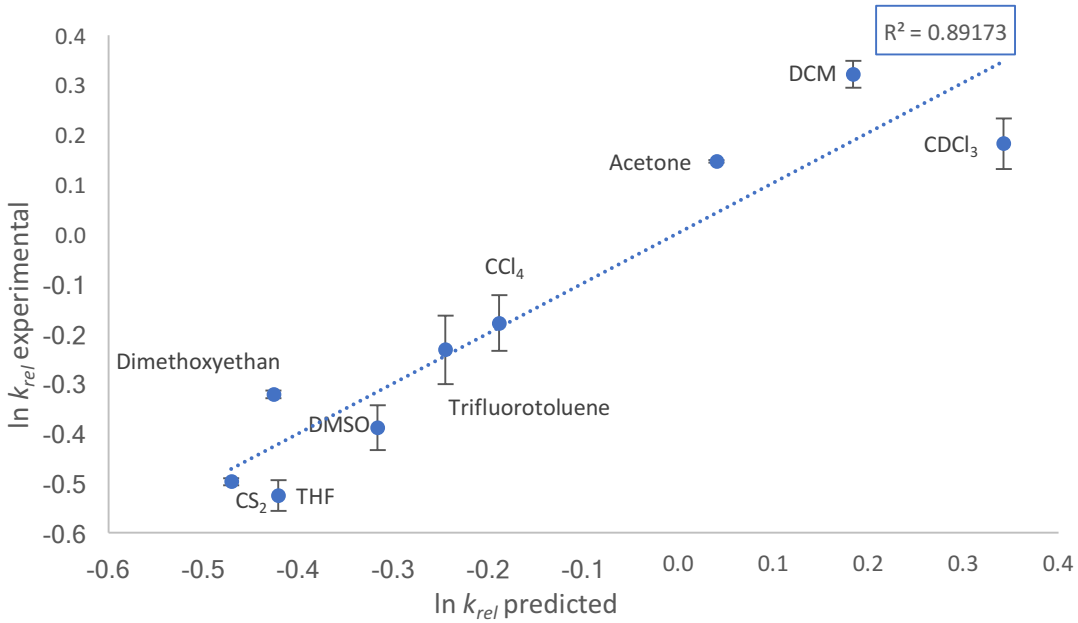


Figure S12: Predicted ln k_{rel} values using Hunter's parameter and Eq. S13 against experimental ln k_{rel} values

Figure S12 shows a good correlation of predicted and experimental ln k_{rel} values. A closer look to Eq. S13 reveals that ln k_{rel} is mainly influenced by its α value, simplifying the discussion by using Fig. 4 of the main text.

As the calculated hydrogen-bond donor ability for aromatic C-H groups was found to be in the range of α=1.0-1.4[9] solvent effects can be explained. If solvent molecules are even worse hydrogen-bond donor than the solvent, hydrogen-bonds arising between solvent and the aromatic C-H-bonds dominate the system. Compared to those solvent-solute interactions attractive solute-solute interactions of the aromatic surfaces of the reactants are minor and their influence on the stability of the transition state is negligible. Particularly the stronger interaction of the napthyl moiety of **2e** and the pyrenyl moiety of alcohol **1f** as compared to alcohol **1a** cannot significantly enhance the rate of the reaction for the bigger system. Moving to solvents with a higher H-bond donor ability makes H-bonds in-between the aromatic C-H-bonds and the solvent less likely leading to desolvation of the solutes and therefore solvent-solvent as well as solute-solute interactions becoming critical. Both, the solvophobic effect of solvent molecules forming hydrogen bonds among each other and the attractive dispersion forces in-between the solutes can then enhance the rate of the reaction. The size of each of those effects depends on the size of the aromatic moieties. For a graphical discussion see

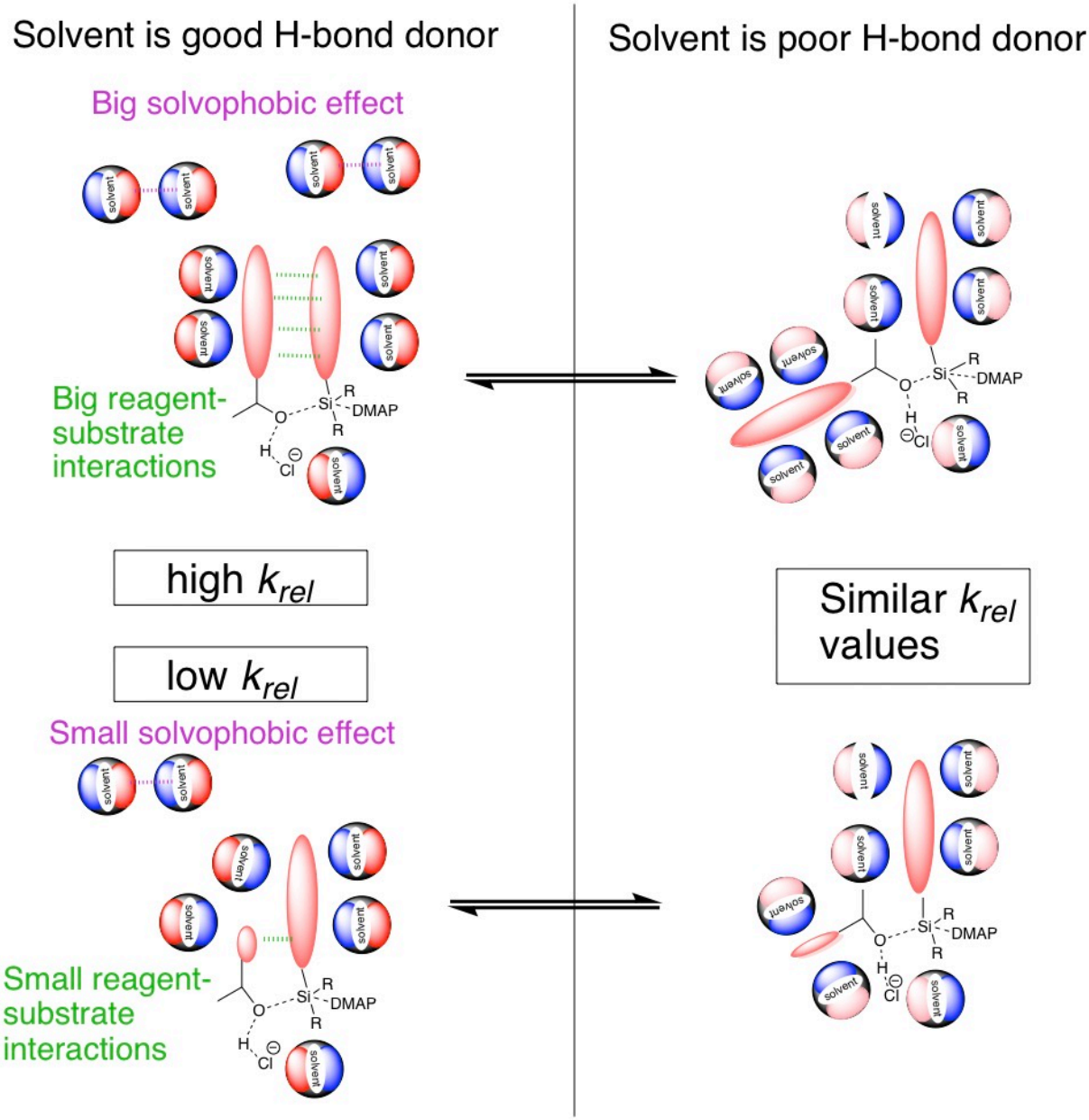


Figure S13: Graphical explanation of solvent effects. Right side: reaction in a solvent with an α value smaller than α of C-H-bonds. Solvent molecules accept H-bonds from the aromatic surfaces and in order to maintain those interactions the transition state is proposed to have a conformation without aromatic overlapping. Therefore, size effects cannot influence k_{rel}. Left side: the solvent is a good hydrogen bond donor itself and prefers interacting with other solvent molecules. Those interactions cause the solvophobic effect but also allows attractive interactions between the aromatic moieties of alcohol and the silyl to take place. Thus, the reaction with the higher degree of aromatic overlapping is enhanced. For solvents with low α a higher ced even pushes the equilibrium further on the right side as solvent-solute interactions get stronger, too. Only in solvents with a high α the discussion about the contribution of solvophobic effect vs. dispersive interactions is senseful. A higher ced strengthens the solvophobic effect, dispersive interactions are temperature independent and can be quantified by computational methods. Those studies show that both effects work together in enhancing reaction rates through size effects.

There is an ongoing discussion if aromatic stacking is caused either mainly by dispersion forces or mainly by solvophobic effects.

Solvophobic effects are the generalized idea of hydrophobic effects. If a molecule with a nonpolar surface is solved in a polar solvent, the dipole-dipole interactions or the hydrogen-bonds of the solvents are disturbed. Therefore, regaining the energy of those intermolecular forces among solvent molecules could be the driving force behind the stacking of non-polar surfaces. This driving force would also grow with bigger aromatic surfaces, as the distortion of the solvent-solvent-interactions gets higher, too.

The solvophobicity is a function of the intermolecular forces among the solvent molecules. Therefore, the ced seems to be the best parameter to predict the solvophobic effect of a solvent, as Cockroft showed by comparing different solvent parameters.[30]

Several studies were carried out to distinguish between solvophobic and dispersive forces:

Iverson showed that the self-association constants of foldamers in various solvent are correlating with the cohesive energy density of the solvents.[31] Those results led him to the conclusion, that at that point there was no experimental evidence, that face-centred π-stacking is a measurable value in solutions, but rather exclusively solvophobic and electrostatic effects drive those stacking.[32]

By using molecular balances with interacting alkyl chains in various solvent, Cockroft showed that those interactions are correlated with the ced of the solvent and therefore mainly caused by solvophobic effects.[33] On the other hand, research on a molecular balance bearing perfluoroalkyl chains in various solvents led to the conclusion that solvophobic effects are dominant in polar solutions, whereas in apolar and florous organic solvents dispersion interactions dominate.[34]

For aromatic systems, Shimizu designed aromatic balances in which the contact surface of the complexes remains constant because one arm of the balance was not changed in size. Through this design he could ensure that the solvophobic effect stayed constant through all the experiments. In this study only relatively minor dispersion contributions to aromatic stacking in solution were found.[35]

To see the effect of solvophobic effects in our reaction design ln k_{rel} of alcohol **1f** compared to **1a** using silyl chloride **2e** were plotted against the cohesive energy density (Figure S14).

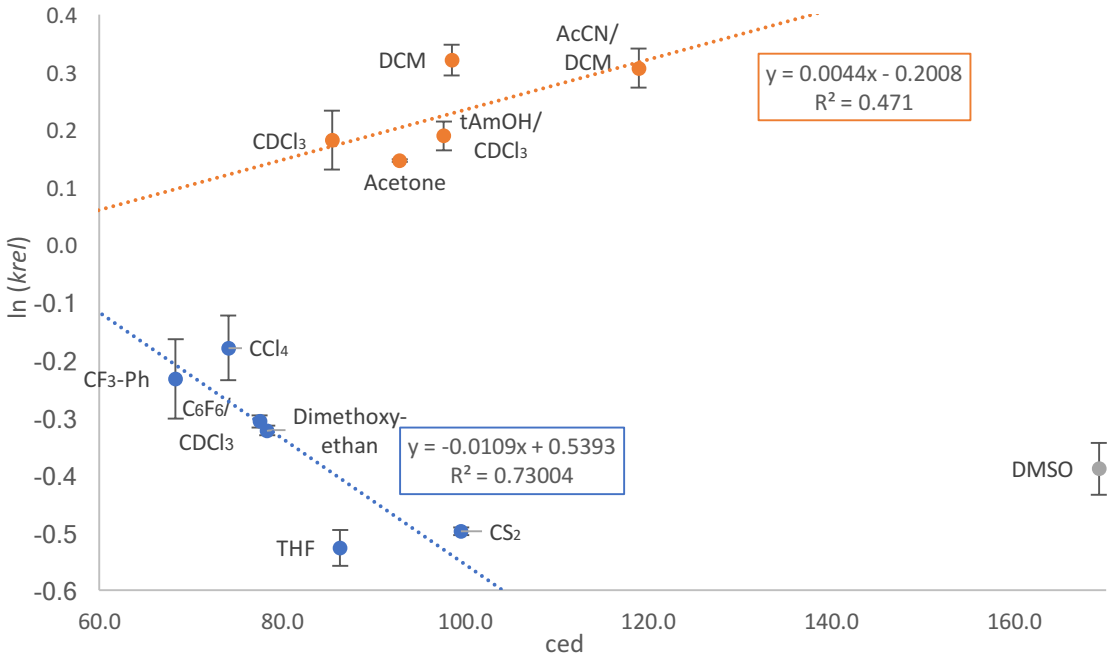


Figure S14: Plot of natural logarithm of relative rate constants of alcohol **1f** compared to **1a** for the Silylation reaction using **2e** against the cohesive energy density.

Solvents were grouped with respect to their hydrogen bond donor ability as the α value is critical in promoting solvent-solute interactions (see discussion above).

On the one hand, in solvents that mainly promote solvent-solute interactions a higher ced is unfavourable for the size-depending rate acceleration, as in a solvent with high ced also unfavourable solvent-solute interactions are strong. For solvents with a higher H-bond donor ability, a positive influence of growing ced on k_{rel} can be observed pointing to the relevance of solvophobic effects in enhancing rates for systems with bigger overlapping surfaces. Still, the low correlation coefficient and the very small slope of the correlation line prove that solvophobic effects alone cannot cause the differences in k_{rel}.

In order to find other solvent influences also other solvent parameters were investigated, but let to no significant correlation (see Table S12). Also for other solvent polarity values like $E_T(30)$-value (Figure S15), Catalán's SdP-Parameter and Hansen's polar parameter no correlation could be found (see Table S12).

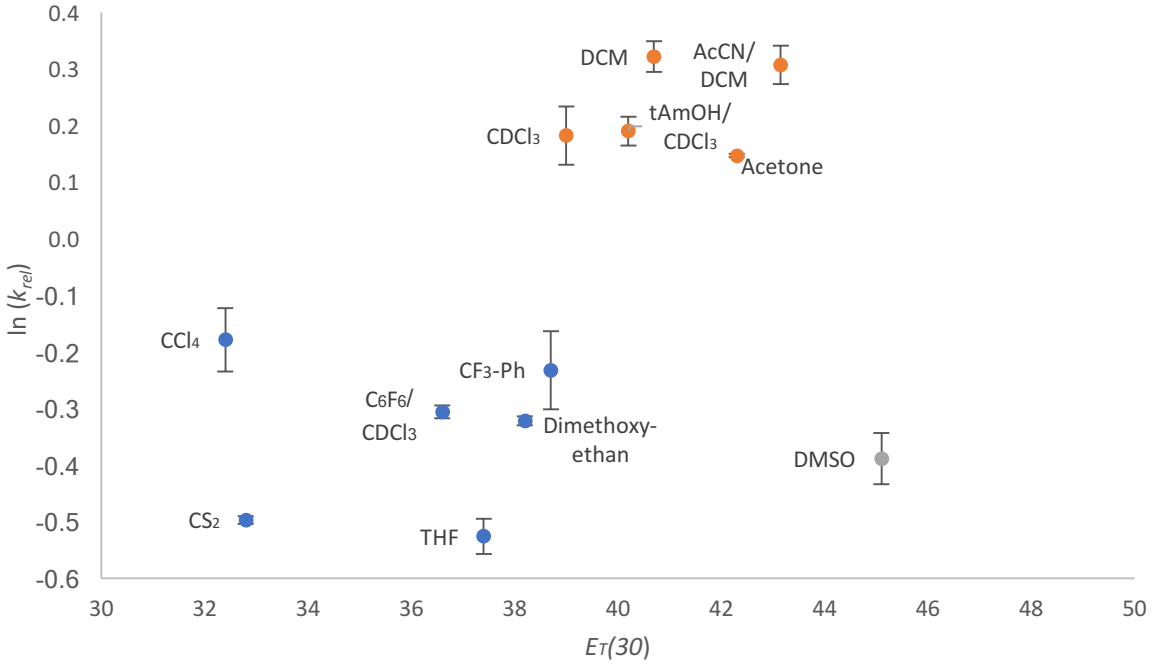


Figure S15: Plot ln k_{rel} of alcohol **1f** compared to **1a** for the Silylation reaction using **2e** against $E_T(30)$.

One problem of measuring dispersion forces in solution is that compared to the gas phase not only dispersion between two reacting molecules is possible but they are competing with solvent-arene dispersion interactions.[33, 34, 36, 37] Those interactions should be stronger the more polarizable the solvent is. Therefore, Catalán's SP-value parameter could describe the strength of those interactions. Figure S16 shows that there is no correlation with. Those results are in accordance with the Kamlet-Taft-analysis, as not dispersive interactions but moreover electrostatic interactions between solvent and solute are the counter player to size-depending interactions.

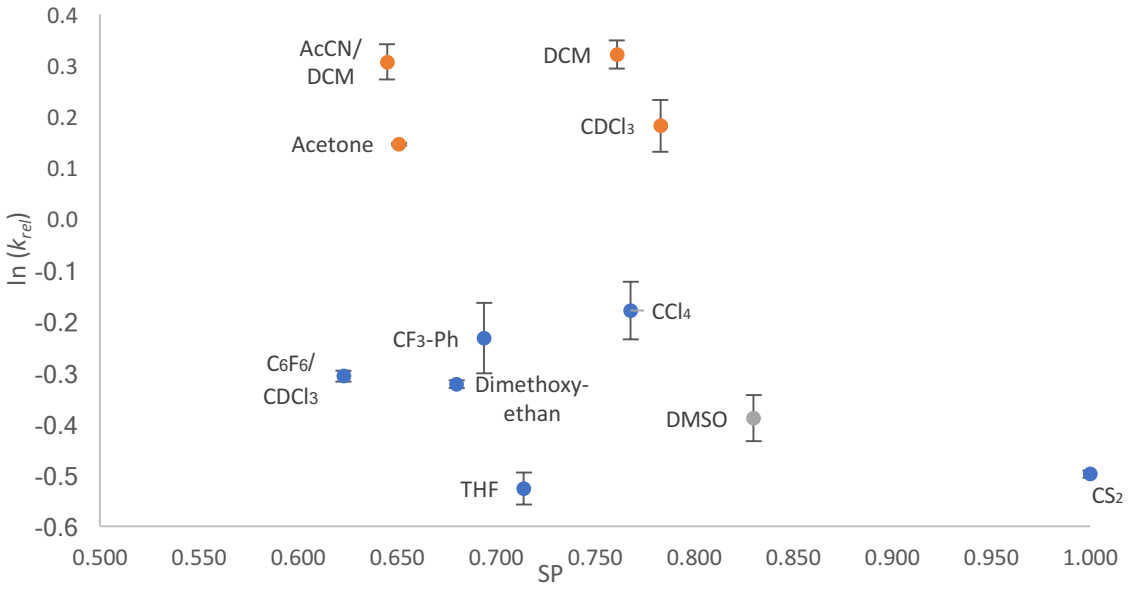


Figure S16: Plot of relative rate constants of alcohol **1f** compared to **1a** for the Silylation reaction using **2e** against solvent bulk polarizability.

Recent studies also proposed an influence of size and shape of the solvent on stacking interactions of polyaromatics.[38] In our study we could observe the trend that small and round-sized solvent molecules seem to be favourable, while rigid and planar molecules disturb aromatic interactions. Further research on the origins of this observation has to be carried out.

4. Investigation of Other Influences on the Rate Constant

4.1. Temperature Effect. Development of Eyring Equation.

As shown in the manuscript, a decrease in temperature is commonly expected to increase selectivity.[39] In the competition experiments that were carried out here, the variation from +23 °C to -10 °C in the temperature of the competition experiment provides small changes in k_{rel} (see Table S13 and Table S14). This translates to a change in the entropy barrier of 7.7 J/K·mol. In order to clarify this entropy variation, the development of the well-known *Eyring* equation Eq. S14 is presented here. As the differences in k_{rel} are that small that they are within the experimental standard deviation, discussion of the calculated entropy barrier would not be reliable.

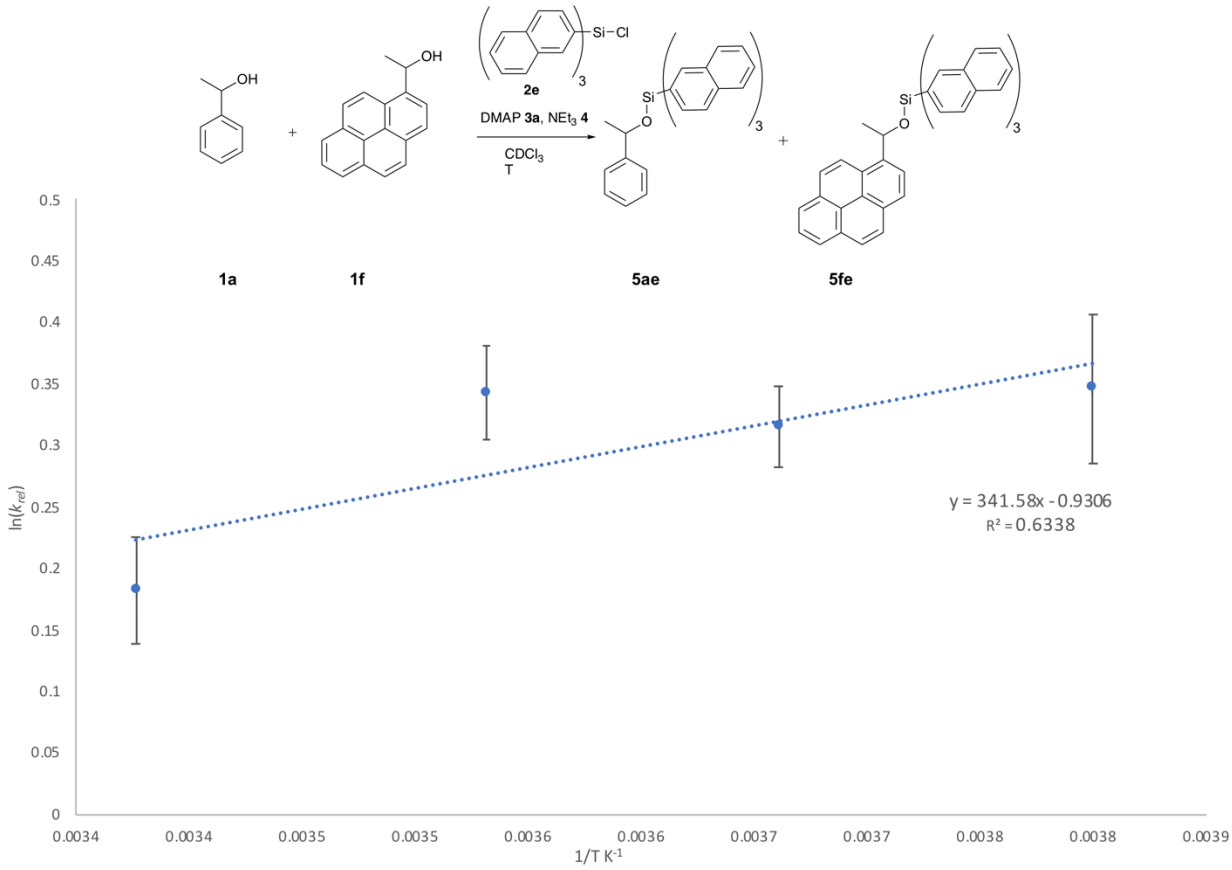


Figure S17: Eyring plot of temperature screening competition experiments.

$$\ln\frac{k_2}{k_1} = \frac{\Delta\Delta H^{\neq}}{R \cdot T} - \frac{\Delta\Delta S^{\neq}}{R} \qquad \text{Eq. S14}$$

Experimental we got:

$$\ln\frac{k_2}{k_1} = \frac{341.58}{T} - 0.9306 \qquad \text{Eq. S15}$$

And taking these terms as:

$$\Delta\Delta H^{\neq} = \Delta\Delta H_2^{\neq} - \Delta\Delta H_1^{\neq}$$

$$\Delta\Delta S^{\neq} = \Delta\Delta S_2^{\neq} - \Delta\Delta S_1^{\neq}$$

$$R = 8.31451\ J/K \cdot mol$$

Next results were calculated,

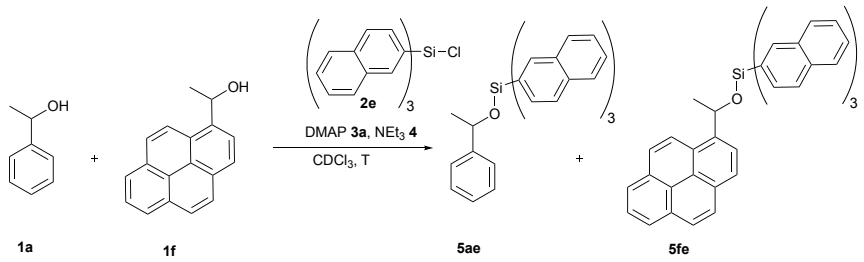
$$\Delta\Delta H^{\neq} = \Delta\Delta H_2^{\neq} - \Delta\Delta H_1^{\neq} = 2840.1\ J/mol = 2.84\ kJ/mol \qquad \text{Eq. S16}$$

$$\Delta\Delta S^{\neq} = \Delta\Delta S_2^{\neq} - \Delta\Delta S_1^{\neq} = 7.73\ J/K \cdot mol \qquad \text{Eq. S17}$$

Table S13: Integral regions and relative integral values for temperature competition experiments of alcohol **1a** and alcohol **1f** using silyl chloride **2e**.

		silyl ether **5fe**			alcohol **1f**			silyl ether **5ae**			alcohol **1a**		
T [K]	**Si-Cl**	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral	Integral region [ppm]		relative integral
263.15	20%	6.11	6.05	1.00	6.02	5.95	6.58	5.07	4.99	0.98	4.92	4.86	6.13
263.15	35%	6.11	6.06	1.00	6.01	5.95	2.70	5.07	4.99	0.99	4.92	4.85	2.51
263.15	50%	6.11	6.05	1.00	6.02	5.96	1.22	5.06	4.99	1.00	4.93	4.86	1.15
263.15	65%	6.12	6.06	1.00	6.03	5.96	0.88	5.06	4.99	1.00	4.93	4.86	0.81
263.15	80%	6.26	6.20	1.00	6.02	5.95	4.33	5.20	5.14	0.72	4.93	4.86	4.31
273.15	20%	6.26	6.21	1.00	6.02	5.95	1.91	5.20	5.14	0.76	4.92	4.87	2.07
273.15	35%	6.27	6.21	1.00	6.02	5.96	1.06	5.21	5.15	0.81	4.93	4.87	1.29
273.15	50%	6.27	6.21	1.00	6.02	5.97	0.57	5.20	5.15	0.81	4.93	4.87	0.84
273.15	65%	6.27	6.21	1.00	6.02	5.97	0.25	5.21	5.15	0.91	4.93	4.88	0.49
283.15	20%	6.26	6.20	1.00	6.02	5.95	4.19	5.20	5.15	0.73	4.93	4.86	4.24
283.15	35%	6.27	6.21	1.00	6.02	5.95	1.87	5.20	5.15	0.75	4.94	4.86	2.05
283.15	50%	6.27	6.21	1.00	6.02	5.96	1.21	5.20	5.14	0.79	4.93	4.87	1.46
283.15	65%	6.27	6.20	1.00	6.02	5.96	0.55	5.21	5.15	0.82	4.94	4.87	0.80
283.15	80%	6.27	6.22	1.00	6.03	5.97	0.29	5.21	5.15	0.93	4.93	4.88	0.53

Table S14: Conversion, corrected chemoselectivity and relative rate constants with standard deviations (derived from five points) calculated from ^{1}H-NMR measurements for temperature depending competition experiments.

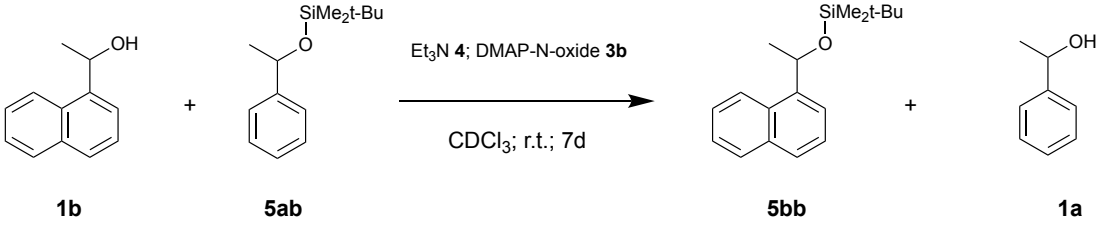


T=263.15 K 1/T=0.003800 K^{-1}		T=273.15 K 1/T=0.003661 K^{-1}		T=283.15 K 1/T=0.003532 K^{-1}	
Conversion (%)	*Chemo-selectivity*	*Conversion (%)*	*Chemo-selectivity*	*Conversion (%)*	*Chemo-selectivity*
0.166	0.134	0.141	0.130	0.170	0.134
0.306	0.122	0.271	0.124	0.309	0.131
0.436	0.114	0.408	0.129	0.401	0.126
0.561	0.128	0.546	0.113	0.575	0.120
0.720	0.103			0.701	0.097
k_{rel} = **1.413**±0.088		k_{rel} =**1.371**±0.045		k_{rel} =**1.408**±0.054	
ln(k_{rel})= 0.346±0.061		ln(k_{rel})= 0.316±0.033		ln(k_{rel})= 0.343±0.038	

T=296.15 K 1/T=0.003377K^{-1}
Exp. data see chapter 1.2
k_{rel} = **1.199**±0.051
ln(k_{rel})= 0.182±0.043

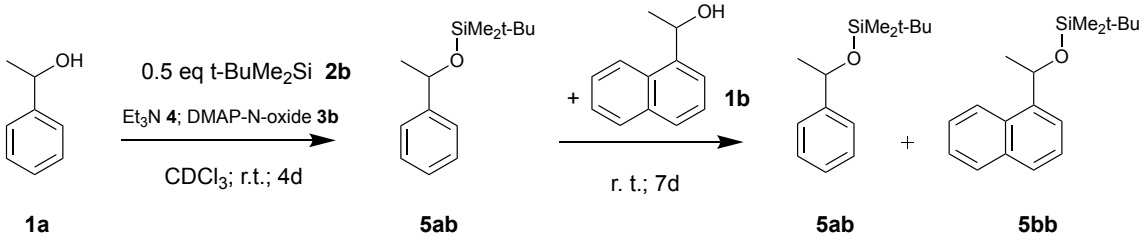
4.2. Transetherification Experiment

Due to long reaction times for some catalysts and substrates the possibility of transetherification (Scheme S5) had to be investigated. This unwanted side reaction would alter the values for the chemoselectivity and selectivity.



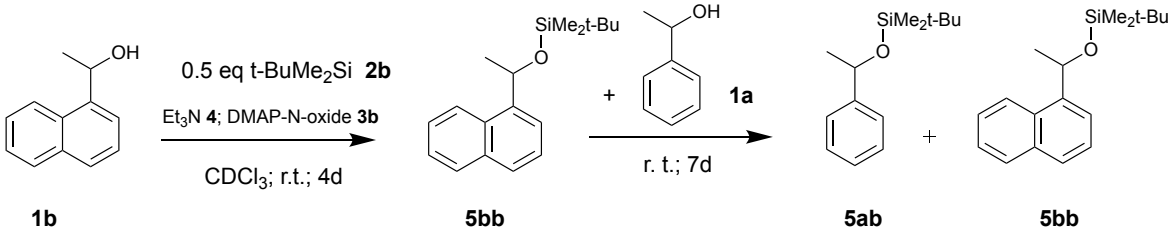
Scheme S5: Possible transetherfication reaction between alcohol **1b** and silyl ether **5ab** under competition experiment conditions.

To verify if transetherfication does happen under competition experiment conditions, a control reaction is done (see Scheme S6). Therefore, 1 eq. of alcohol **1a** and 0.5 eq. of silylation agent TBDMSCl **2b** were put to reaction under competition experiment conditions in a GC-vial to form the silylation product **5ab**. After full reaction, a ^{1}H-NMR spectrum was recorded. Now the alcohol **1b** was added to the mixture and after seven days another ^{1}H-NMR spectrum was recorded.



Scheme S6: Transetherfication experiment starting by a mixture of alcohol **1a** and silyl ether **5ab** adding alcohol **1b**.

The experiment was repeated in the reversed order, so alcohol **1a** was added to a mixture of **1b** and **5bb** (see Scheme S7, Figure S19).



Scheme S7: Transetherfication experiment starting by a mixture of alcohol **1b** and silyl ether **5bb** adding alcohol **1a**.

The NMR-spectra (Figure S18 and Figure S19) show clearly that after addition of the competing alcohol no corresponding silyl ether was formed.

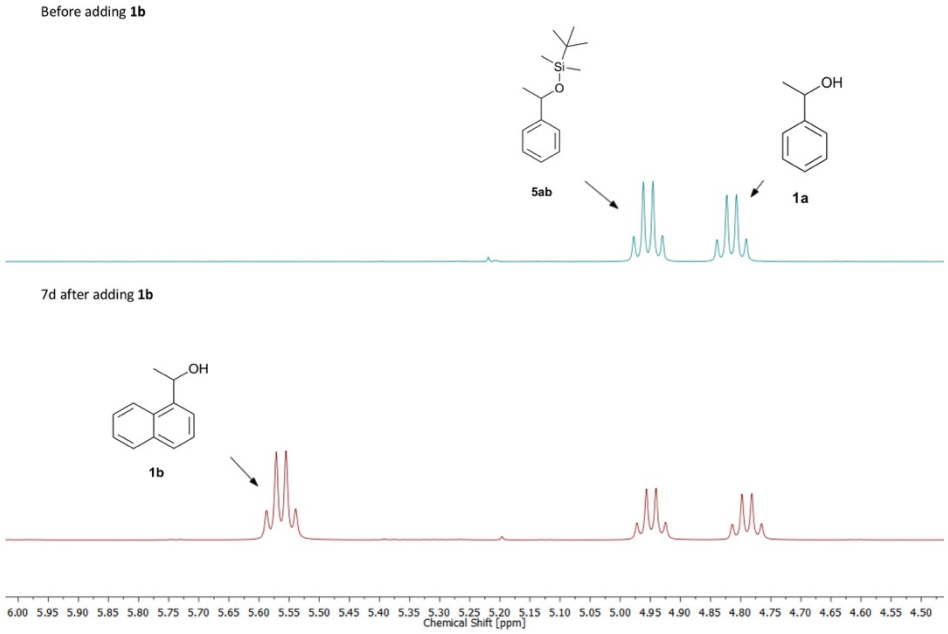


Figure S18: NMR spectra of transetherfication experiment shown in Scheme S6.

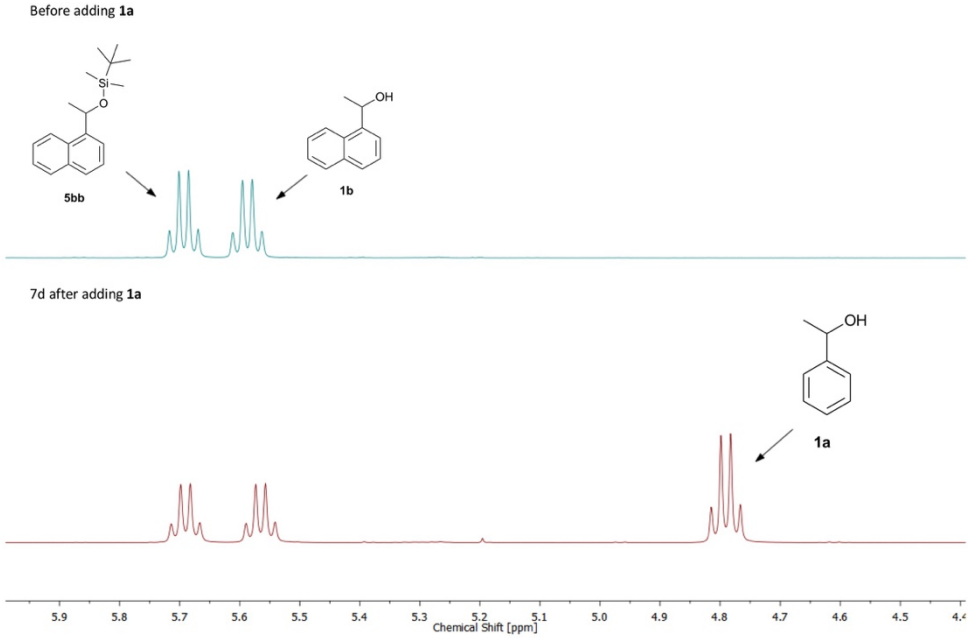


Figure S19: NMR spectra of transetherfication experiment shown in Scheme S7.

With those results in hand, it can be stated that under the conditions of competition experiments no transetherfication takes place. Therefore, the selectivity values and relative rate constants are valid and differences in product ratios originate from the kinetics of the investigated reactions.

5. Synthetic Data

5.1. General Experimental and Analytical Information and Techniques

General Methods: All reactions sensitive to air and moisture were proceeded under a nitrogen atmosphere and the glassware as well as magnetic stir bars were dried overnight in a dry oven at 110°C.

Solvents: If not further specified, solvents were obtained from the companies Acros Organics, Sigma Aldrich, Fluka or Merck and purified by distillation in a rotary evaporator. $CDCl_3$, triethylamine Et_3N **4** and DCM were freshly distilled from calcium hydride (CaH_2) under nitrogen atmosphere.

THF, DCM-d_2, DMSO-d_6 and Acetone-d_6 for solvent competition experiments were purchased "extra-dry" and used without further purification. CCl_4 was freshly distilled from molecular sieve (4 Å), CS_2 from $MgSO_4$ and dimethoxyethan from sodium, all of them were stored over molecular sieve (4 Å).

Reagents and Catalysts: All reagents were purchased from the companies TCI, Sigma Aldrich or Acros and used without further purification, if not mentioned otherwise. All air- or water-sensitive reagents were stored under nitrogen.

Chromatography: Silica gel for column chromatography was purchased from Acros Organics (mesh 35-70). Thin-layer chromatograpy was performed by using TLC plates purchased by Merck (silica gel 60 F254, thickness 0.2 mm). Preparative layer chromatography (PLC) was carried out by using Merck TLC glass plates (silica gel 60 F254, thickness 2 mm).

NMR spectroscopy: All ^{1}H-NMR spectra were recorded by Varian INOVA 400 and 600 machines in $CDCl_3$ or DMSO at 400 MHz or 600MHz at 23 °C. All ^{13}C-NMR spectra were recorded respectively at 101 MHz and 151 MHz. The ^{29}Si-NMR spectra were recorded with Bruker 400 TR or JEOL 400 machine at 79 MHz. The chemical shifts are reported in ppm (δ), relative to the resonance of $CDCl_3$ at δ = 7.26 ppm for ^{1}H and for ^{13}C relative to the resonance of $CDCl_3$ δ = 77.16 ppm. Spectra were imported and processed in the MestreNova 10.0.2 program. Peaks were assigned using HSQC-spectra.

Mass spectroscopy: HRMS spectra were obtained by using a Thermo Finnigan LTQ FT machine of the MAT 95 type with a direct exposure probe (DEP) and electron impact ionization (EI, 70 eV).

X-ray crystallography: crystallographic measurements were done using an Oxford Diffraction XCalibur with Saphir CCD-detector and a molybdenum-K_α–source (λ = 0.71073 Å) with concentric circle kappa-device. Structures were resolved using SHELXS or SIR97 and refined with SHELXS.

Melting points: melting point were measure at a Stuart SMP10 and are stated uncorrected.

5.2. Synthetic Procedures and Compound Characterization

Synthesis of Silyl Chlorides

General Procedure 1 for the Grignard-synthesis of Silanes (GP1)

In an oven-dried three-neck-flask 2 eq magnesium-turnings and anhydrous LiCl (1.1 eq) were heated to 600 °C under high vacuum for 5 minutes. After flushing with nitrogen and cooling down, magnesium turnings were covered with dry THF. 1 eq of the corresponding bromoarene was dissolved in dry THF and $\frac{1}{10}$ of this solution was added to the flask. After the reaction started, the rest of the solution was slowly dropped in over approx. 30 min. The solution was then stirred for another 30 min at room temperature.

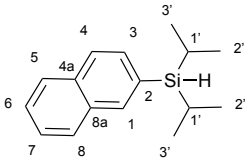
The corresponding amount of chlorosilane in dry THF was added slowly under ice-cooling and then refluxed for 3 hours.

The reaction mixture was quenched with ice water, then HCl (aq) was added until all $Mg(OH)_2$ was solved. The reaction mixture was extracted with EtOAc (1x 20mL) and with DCM (2x 20mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified through recrystallizations or distillation.

General Procedure for Chlorination of Silanes[40] (GP2)

In an oven dried 50 mL Schlenk-flask the silane was dissolved in dry CCl_4 under nitrogen at room temperature. SO_2Cl_2 was added via syringe and the solution was refluxed. After full conversion (monitored by the disappearance of the silane-H via ^{1}H-NMR) solvent and excess reagents were evaporated under vacuum (extra cooling trap is used). The residue was purified by recrystallization or distillation.

Diisopropyl(naphthalen-2-yl)silane **7c**

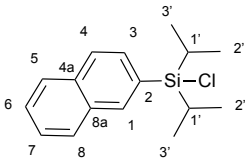


$$6c

Diisopropyl(naphthalen-2-yl)silane **7c** was synthesized according to GP1 starting from magnesium-turnings (240 mg, 10.0 mmol), LiCl (252 mg, 6.00 mmol) and 2-bromonaphtalene (1.04 g, 5.00 mmol) in 5 mL of THF. Chlorodiisopropylsilane (754 mg, 5.00 mmol) in 2 mL THF was added. Kugelrohr-distillation yielded in **7c** (890 mg,

3.68 mmol, 73.5%) as a colorless oil with a boiling point of 156 °C (1 mbar). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (1H, s, 1-H), 8.06 – 8.01 (1H, m, 4-H), 7.99 (2H, d, *J* = 7.2 Hz, 5-H, 8-H), 7.84 – 7.76 (1H, m, 3-H), 7.69 – 7.60 (2H, m, 6-H, 7-H), 4.35 – 4.31 (1H, m, Si-*H*), 1.57 – 1.44 (2H, m, 1'-H), 1.29 (12H, ddt, *J* = 30.1, 7.3, 1.8 Hz, 2'-H, 3'-H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.60 (C1), 134.01 (s), 133.14 (s), 131.92 (s), 131.67 (C2), 128.20, 127.89, 126.95, 126.46, 125.99, 18.93 (CH_3), 18.76 (CH_3), 11.03 (C*H*-CH_3). **^{29}Si NMR** (53.7 MHz, $CDCl_3$) δ 7.16. **HRMS** (70 eV, EI) m/z calc. for $C_{16}H_{22}Si$ $[M]^+$ 242.1491; found 242.1484.

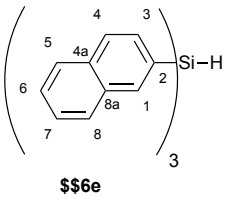
Chlorodiisopropyl(naphthalen-2-yl)silane **2c**



2c

Chlorodiisopropyl(naphthalen-2-yl)silane **2c** was synthesized according to GP2 with 760 mg (3.14 mmol) of diisopropyl(naphthalen-2-yl)silane **7c** and 466 mg (3.45 mmol) of SO_2Cl_2 in 5 mL of CCl_4. Refluxing for 5 hrs and Kugelrohr-distillation yielded in 589 mg of **2c** (2.13 mmol, 67.9%) with a boiling point of 169 °C (1mbar). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (1H, s, 1-H), 7.96 – 7.86 (3H, m, 4-H, 5-H, 8-H), 7.69 (1H, d, *J* = 8.2 Hz, 3-H), 7.60 – 7.51 (2H, m, 6-H, 7-H), 1.55 (2H, hept, *J* = 7.3 Hz, 1'-H), 1.18 (6H, d, *J* = 7.3 Hz, 2'-H), 1.10 (6H, d, *J* = 7.4 Hz, 3'-H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.80, 134.25 (s), 132.88 (s), 130.07 (s), 129.87, 128.49, 127.86, 127.24, 127.04, 126.27, 17.24 (CH_3), 16.98 (CH_3), 14.09 (C*H*-CH_3). **^{29}Si NMR** (53.7 MHz, $CDCl_3$) δ 27.88. **HRMS** (70 eV, EI) m/z calc. for $C_{16}H_{22}ClSi$ $[M]^+$ 276.1101; found 276.1091.

Tri(naphthalen-2-yl)silane **7e**



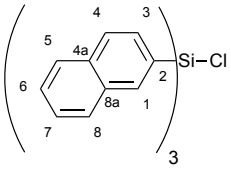
$$6e

Tri(naphthalen-2-yl)silane **7e** was synthesized according GP1 using magnesium-turnings (2.40 g, 100 mmol), anhydrous LiCl (2.33 g, 55.0 mmol), 2-bromonaphtalene (10.4 g, 50 mmol) in 20 mL of THF and trichlorosilane (2.03 g, 15.0 mmol) in 5 mL of THF.

A white powder was obtained through twice recrystallization from a 4:1-mixture of *iso*-hexane and ethyl acetate (4.90 g, 11.9 mmol, 79.5%), **mp** 144-146 °C. **Elemental analysis:** Found: C, 87.3; H, 5.4. Calc. for $C_{30}H_{22}Si$: C, 87.8; H, 5.4%; **^{1}H NMR** (400 MHz; $CDCl_3$) δ 8.24 (3H, s, 1-H), 7.95 – 7.88 (6H, m, 5-H, 8-H), 7.85 (3H, d, *J* = 7.9 Hz, 4-H), 7.77 (3H, d, *J* = 8.1 Hz, 3-H), 7.60 – 7.49 (6H, m, 6-H, 7-H), 5.98 – 5.85 (1H, m, Si-*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.43

(C1), 134.28 (s), 133.18 (s), 131.59 (C3), 130.87 (s), 128.40 (C4), 127.94, 127.60, 127.02, 126.26. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -16.95. **HRMS** (70 eV, EI) m/z calc. for $C_{30}H_{22}Si$ $[M]^+$ 410.1491; found 410.1482.

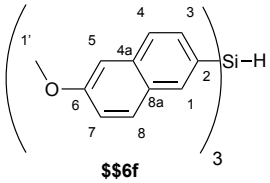
Chlorotri(naphthalen-2-yl)silane **2e**



2e

Chlorotri(naphthalen-2-yl)silane **2e** was synthesized following GP2 using tri(naphthalen-2-yl)silane **7e** (2.05 g, 5.00 mmol) in 20 mL of dry CCl_4 and 1.35 g of SO_2Cl_2 (10 mmol). The product was recrystallized from *iso*-Hexane/DCM (11:7) and Schlenk filtrated to yield in chlorotri(naphthalen-2-yl)silane **2e** (1.22 g, 2.70 mmol, 55.0%), **mp** 180 – 182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (3H, s, 1-H), 7.95 – 7.87 (6H, m, 5-H, 8-H), 7.84 (3H, d, *J* = 8.1 Hz, 4-H), 7.80 (3H, dd, *J* = 8.2, 1.2 Hz, 3-H), 7.60 – 7.49 (6H, m, 6-H, 7-H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.25, 134.64 (s), 132.91 (s), 130.58, 130.39 (s), 128.75, 127.97, 127.84, 127.60, 126.51. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -2.76. **HRMS** (70 eV, EI) m/z calc. for $C_{30}H_{21}ClSi$ $[M]^+$ 444.1101; found 444.1104.

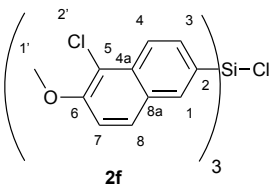
Tris(6-methoxynaphthalen-2-yl)silane **7f**



$$6f

Tris(6-methoxynaphthalen-2-yl)silane **7f** was synthesized according to GP1 using magnesium-turnings (2.40 g, 100 mmol), anhydrous LiCl (2.33 g, 55.0 mmol), 2-bromo-6-methoxynaphtalene (11.9 g, 50.0 mmol) in 35 mL of THF and trichlorosilane (2.03 g, 7.50 mmol) in 5 mL of THF. After quenching, the precipitated product was filtered out, solved in hot $CHCl_3$, hot filtrated to remove remaining magnesium turnings and recrystallized. The filtrate was treated as described in general procedure 1, the crude product was then recrystallized from $CHCl_3$. Combining the purified products led to 7.50 g (14.9 mmol, 99.0%) of **7f** as a white powder, **mp** 132-134 °C. **^{1}H NMR** (400 MHz; $CDCl_3$) δ 8.07 (3H, s, 1-H), 7.76 (3H, d, *J* = 8.2 Hz, 8-H), 7.72 – 7.68 (3H, m, 4-H), 7.66 (3H, dd, *J* = 8.2, 1.1 Hz, 3-H), 7.15 (3H, s, 5-H), 7.17 – 7.12 (3H, m, 7-H), 5.79 (1H, s, Si-*H*), 3.93 (9H, s, 1'-H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.52 (s, C6), 137.03 (C1), 135.56 (s), 132.35 (C3), 129.99 (C4), 128.83 (s), 128.38 (s), 126.50 (C8), 119.02 (C7), 105.82 (C5), 55.50 (C1'). **HRMS** (70 eV, EI) m/z calc. for $C_{33}H_{28}O_3Si$ $[M]^+$ 500.1808; found 500.1795.

Chlorotris(7-chloro-6-methoxynaphthalen-2-yl)silane **2f**



2f

Chlorotris(7-chloro-6-methoxynaphthalen-2-yl)silane **2f** was synthesized following GP2 using Tris(6-methoxynaphthalen-2-yl)silane **7e** (1.40 g, 2.80 mmol) in 15 mL of dry CCl_4 and 1.51 g of SO_2Cl_2 (11.2 mmol). The product was recrystallized from *iso*-Hexane/DCM and Schlenk filtrated to yield in **2f** (1.14 g, 1.79 mmol, 64%), **mp** 175-177 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (3H, d, *J* = 8.6 Hz, 4-H), 8.12 (3H, s, 1-H), 7.84 (3H, dd, *J* = 8.6, 1.2 Hz, 3-H), 7.77 (3H, d, *J* = 8.9 Hz, 8-H), 7.33 (3H, d, *J* = 9.1 Hz, 7-H), 4.06 (9H, s, 1'-H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.91 (s, C6), 137.32 (C1), 133.22 (s), 132.04 (C4), 128.99 (C8), 128.94 (s), 128.26 (s), 123.49 (C4), 116.93 (s, C5), 113.96 (C7), 57.04 (C1'). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 2.56. **HRMS** (70 eV, EI) m/z calc. for $C_{33}H_{24}Cl_4O_3Si$ $[M]^+$ 636.0249; found 636.0233.

Synthesis of Alcohols

General Procedures for the Preparation of Secondary Alcohols (GP3)

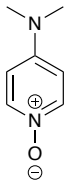
The aryl ketone was solved in 30 mL of methanol and cooled to 0 °C. $NaBH_4$ was added slowly and the reaction mixture was stirred for 3 hours. The solution was extracted with dichloromethane (3 x 15 mL) and washed with brine. Then the product was precipitated through addition of n-hexane.

Alcohol **1d**[41] and **1e**[42] were synthesized following GP3 and characterised by ^{1}H-NMR, ^{13}C-NMR and HRMS in accordance with the literature.

Alcohol **1f** was synthesized from the corresponding aldehyde according to the literature.[43]

Synthesis of catalyst

4-Dimethylaminopyridine-N-oxide **3c**


3c

4-Nitropyridine-N-Oxide (3.55 g, 25.4 mmol) was dissolved in acetyl chloride (30 mL) and the resulting reaction mixture was refluxed for 2.5h. After removing excess acetyl chloride at reduced pressure, the crude product was poured into a mixture of ice (50 g) and a saturated aq. solution of $NaHCO_3$. The reaction mixture was extracted with dichloromethane (10 x 30 mL), dried over anhydrous

$MgSO_4$ and the solvent was removed under vacuo. Washing with n-hexane yielded in 76% of 4-chloropyridine-N-oxide (2.51 g, 18.38 mmol).

The 4-chloropyridine-N-oxide (1.5 g, 11.58 mmol) was then dissolved in dimethylamine (4.5 mL, 40%wt aq. sol.) and radiated in a microwave for 1h at 110 °C. The reaction mixture was conc. in vacuo (toluene used to azeotrope water), dissolved in dichloromethane (10 mL), washed with sat. sodium carbonate (5 mL) and extracted with DCM (10 x 20 mL). The combined organic layers were then dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the product was washed with n-hexane to afford 98% (1.57 g, 11.35 mmol) of DMAP-N-oxide **3c** as a light brown solid.

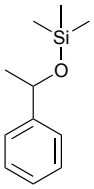
DMAP-N-oxide **3c** was characterized according to the literature.[44]

Synthesis of silyl ethers

General procedure for the synthesis of silyl ethers (GP4)

0.15 mmol of the alcohol and 0.023 mmol of DMAP **3a** were solved in 5 mL of anhydrous DCM in an oven-dried flask under N_2. 0.18 mmol of NEt_3 **4** and 0.18 mmol of the corresponding silyl chloride were added, the reaction was stirred and monitored via TLC. After full conversion, the reaction mixture was washed with $NaHCO_3$ (1x 5 mL), the solvent was evaporated under reduced pressure and the crude residue was purified by preparative TLC. Yields were calculated from competition experiment NMRs regarding the silyl chloride conversion.

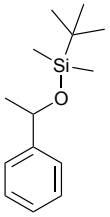
Trimethyl(1-phenylethoxy)silane **5aa**[45]



5aa

Synthesized according to GP4 using **1a** and **2a** yielding in a colourless oil (84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (4H, m, Ar-*H*), 7.25 – 7.20 (1H, m, Ar-*H*), 4.86 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.44 (3H, d, *J* = 6.4 Hz, O-CH-CH_3), 0.08 (9H, s, Si-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.60 (s), 128.28, 126.98, 125.50, 70.74 (O-*C*H), 27.02 (O-CH-*C*H_3), 0.26 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -17.27. **HRMS** (70 eV, EI) m/z calc. for $C_{11}H_{18}OSi$ $[M-H]^+$ 193.1049; found 193.1044; calc. for $[M-CH_3]^+$ 179.0892; found 179.0885.

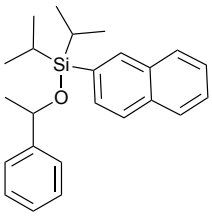
tert-Butyldimethyl(1-phenylethoxy)silane **5ab**



5ab

Synthesized according to GP4 using **1a** and **2b** yielding in a colourless oil (87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (4H, m, Ar-*H*), 7.30 – 7.20 (1H, m, Ar-*H*), 4.91 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.45 (3H, d, *J* = 6.3 Hz, O-CH-CH_3), 0.94 (9H, s, Si-C-CH_3), 0.09 (3H, s, Si-CH_3), 0.01 (3H, s, Si-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.94 (s), 128.06, 126.66, 125.18, 70.82 (O-*C*H), 27.29 (O-CH-*C*H_3), 25.89 (Si-C-*C*H_3), 18.28 (s, Si-*C*-CH_3), -4.78 (Si-*C*H_3), -4.82 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 18.14. **HRMS** (70 eV, EI) m/z calc. for $C_{14}H_{24}OSi$ $[M\text{-}CH_3]^+$ 221.1362; found: 221.1349, $[M\text{-}tBu]^+$ 179.0892 found; 179.0880.

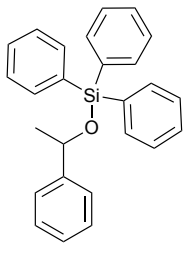
Diisopropyl(naphtalen-2-yl)(1-phenylethoxy)silane **5ac**



5ac

Synthesized according to GP4 using **1a** and **2c** yielding in a colourless oil (75%). **R_f** 0.67 (*i*Hex:EtOAc=19:1) . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (1H, s, Ar-*H*), 7.86 – 7.72 (3H, m, Ar-*H*), 7.59 (1H, d, *J* = 8.1 Hz, Ar-*H*), 7.52 – 7.44 (2H, m, Ar-*H*), 7.42 (2H, d, *J* = 7.5 Hz, Ar-*H*), 7.35 (2H, t, *J* = 7.6 Hz, Ar-*H*), 7.31 – 7.26 (1H, m, Ar-*H*), 5.06 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.55 (3H, d, *J* = 6.3 Hz, O-CH-CH_3), 1.37 (2H, hept, *J* = 7.4 Hz, iPr-C*H*), 1.08 – 0.98 (12H, m, iPr-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.10 (s), 135.91, 133.96 (s), 132.90 (s), 132.52 (s), 131.05, 128.41, 128.32, 127.78, 127.05, 126.68, 126.47, 125.81, 125.54, 71.90 *(*O-*C*H), 27.94 (O-CH-*C*H_3), 17.65 (iPr-*C*H_3), 17.59 (iPr-*C*H_3), 17.52 (iPr-*C*H_3), 17.42 (iPr-*C*H_3), 12.65 (iPr-*C*H), 12.54 (iPr-*C*H). **HRMS** (70 eV, EI) m/z calc. for $C_{24}H_{30}OSi$ $[M]^+$ 362.2066; found 362.2046.

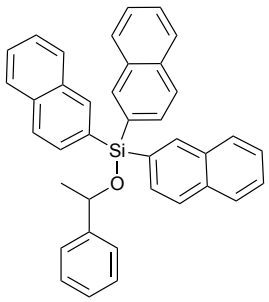
Triphenyl(1-phenylethoxy)silane **5ad**[46]



5ad

Synthesized according to GP4 using **1a** and **2d** yielding in a colourless oil (95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (6H, m, Ar-*H*), 7.51 – 7.44 (3H, m, Ar-*H*), 7.44 – 7.37 (8H, m, Ar-*H*), 7.37 – 7.31 (2H, m, Ar.*H*), 7.30 – 7.26 (1H, m, Ar-*H*), 5.11 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.50 (3H, d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.99 (s), 135.51, 134.62 (s), 129.96, 128.16, 127.81, 126.91, 125.51, 72.06 (O-*C*H), 26.96 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -13.21. **HRMS** (70 eV, EI) m/z calc. for $C_{26}H_{24}OSi$ $[M]^+$ 380.1596; found 380.1596.

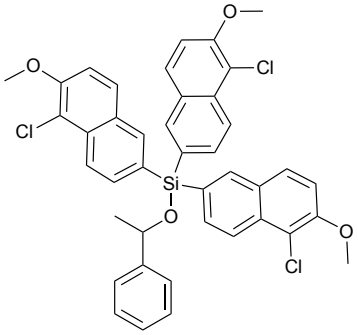
Tri(naphtalen-2-yl)(1-phenylethoxy)silane **5ae**



5ae

Synthesized according to GP4 using **1a** and **2e** yielding in a colourless liquid (88%). $\mathbf{R_f}$ 0.65 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (3H, s, Ar-*H*), 7.86 (6H, dd, J = 8.0, 3.9 Hz, Ar-*H*), 7.80 – 7.73 (6H, m, Ar-*H*), 7.57 – 7.45 (6H, m, Ar-*H*), 7.44 – 7.39 (2H, m, Ar-*H*), 7.34 – 7.24 (3H, m, Ar-*H*), 5.19 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.54 (3H, d, *J* = 6.3 Hz, O-CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.08 (s), 137.17, 134.36, 132.97, 132.18, 131.26, 128.64, 128.36, 127.88, 127.27, 127.20 (s), 127.02, 126.10, 125.82, 72.57 (O-*C*H), 27.12 (O-CH-*C*H$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.15. **HRMS** (70 eV, EI) m/z calc. for $C_{38}H_{30}OSi$ $[M]^+$ 530.2066; found 530.2060.

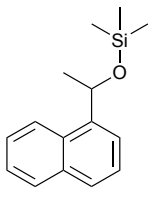
Tris(5-chloro-6-methoxynaphthalen-2-yl)(1-phenylethoxy)silane **5af**



5af

Synthesized according to GP4 using **1a** and **2f** yielding in a brown oil (84%). $\mathbf{R_f}$ 0.78 (*i*Hex:EtOAc=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (3H, d, *J* = 8.5 Hz, Ar-*H*), 8.02 (3H, s, Ar-*H*), 7.77 (3H, dd, *J* = 8.5, 1.1 Hz, Ar-*H*), 7.64 (3H, d, *J* = 9.0 Hz, Ar-*H*), 7.35 (2H, dd, *J* = 8.2, 1.2 Hz, Ar-*H*), 7.29 – 7.19 (6H, m, Ar-*H*), 5.12 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 4.00 (9H, s, O-C*H*$_3$), 1.49 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.51 (s), 145.89 (s), 137.25, 132.90 (s), 132.74, 130.08, 129.09, 128.83, 128.41, 127.31 (s), 125.81, 122.92, 116.88 (s), 113.71, 72.69 (O-C*H*), 57.05 (O-C*H*$_3$), 27.07 (O-CH-*C*H$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.22. **HRMS** (70 eV, EI) m/z calc. for $C_{41}H_{33}Cl_3O_4Si$ $[M]^+$ 722.1214; found 722.1219.

Trimethyl(1-(naphthalen-1-yl)ethoxy)silane **5ba**[47]

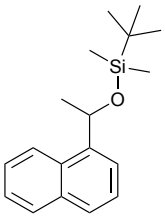


5ba

Synthesized according to GP4 using **1b** and **2a** yielding in a colourless oil (97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (1H, d, *J* = 8.3 Hz, Ar-*H*), 7.93 (1H, d, *J* = 7.9 Hz, Ar-*H*), 7.82 – 7.75 (2H, m, Ar-*H*), 7.59 – 7.49 (3H, m, Ar-*H*), 5.68 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.77 – 1.57 (3H, m, *J* = 6.3 Hz, O-CH-C*H*$_3$), 0.17 (9H, s, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.27 (s), 133.80 (s), 129.96 (s), 128.90, 127.36, 125.64, 125.60, 125.24, 123.32, 122.80, 68.18 (O-*C*H), 26.54 (O-CH-

CH_3), 0.16 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -17.36. **HRMS** (70 eV, EI) m/z calc. for $C_{15}H_{20}OSi$ $[M]^+$ 244.1283; found 244.1277.

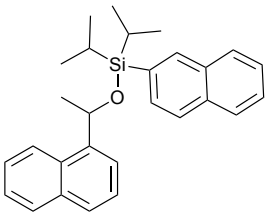
tert-Butyldimethyl (1-(naphthalen-1-yl)ethoxy)silane **5bb**



5bb

Synthesized according to GP4 using **1b** and **2b** yielding in a colourless oil (89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (1H, d, *J* = 8.3 Hz, Ar-*H*), 7.88 (1H, d, *J* = 7.8 Hz, Ar-*H*), 7.75 (1H, d, *J* = 8.2 Hz, Ar-*H*), 7.71 (1H, d, *J* = 7.2 Hz, Ar-*H*), 7.53 – 7.45 (3H, m, Ar-*H*), 5.61 (1H, q, *J* = 6.2 Hz, O-C*H*-CH_3), 1.59 (3H, d, *J* = 6.2, O-CH-C*H*$_3$), 0.97 – 0.93 (9H, m, Si-C-C*H*$_3$), 0.09 (3H, d, *J* = 1.7 Hz, Si-C*H*$_3$), -0.02 (3H, d, *J* = 1.7 Hz, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.69 (s), 133.88 (s), 130.00 (s), 128.99, 127.34, 125.73, 125.69, 125.31, 123.50, 122.83, 68.66 (O-*C*H), 26.79 (O-CH-*C*H_3), 26.06 (Si-C-*C*H_3), 18.47 (s, Si-*C*-CH_3), -4.65 (Si-*C*H_3), -4.74 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ –18.48. **HRMS** (70 eV, EI) m/z calc. for $C_{18}H_{28}OSi$, $[M-CH_3]^+$ 271.1518 found; 271.1505, $[M-tBu]^+$ 229.1049; found: 229.1033.

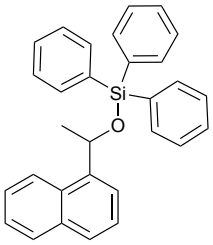
Diisopropyl(naphtalen-2-yl)(1-(naphthalen-1-yl)ethoxy)silane **5bc**



5bc

Synthesized according to GP4 using **1b** and **2c** yielding in a colourless oil (85%). **R_f** 0.64 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (1H, m, Ar-*H*), 8.03 (1H, s, Ar-*H*), 7.91 – 7.87 (1H, m, Ar-*H*), 7.86 – 7.75 (4H, m, Ar-*H*), 7.68 (1H, d, *J* = 7.8 Hz, Ar-*H*), 7.61 (1H, dd, *J* = 8.2, 1.0 Hz, Ar-*H*), 7.54 – 7.42 (5H, m, Ar-*H*), 5.80 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.71 (3H, d, *J* = 6.3 Hz, O-CH-C*H*$_3$), 1.40 (2H, m, Si-C*H*-CH_3), 1.09 – 0.97 (12H, m, Si-CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.70 (s), 135.92, 133.96 (s), 133.90 (s), 132.91 (s), 132.43 (s), 131.00, 129.94 (s), 128.98, 128.38, 127.76, 127.53, 126.74, 126.48, 125.81, 125.79, 125.73, 125.38, 123.52, 123.18, 69.45 (O-*C*H), 27.12(O-CH-*C*H_3), 17.66 (iPr-*C*H_3), 17.64 (iPr-*C*H_3), 17.55 (iPr-*C*H_3), 17.46 (iPr-*C*H_3), 12.72 (iPr-*C*H), 12.56 (iPr-*C*H). **HRMS** (70 eV, EI) m/z calc. for $C_{28}H_{32}OSi$ $[M]^+$ 412.2222; found 412.2226.

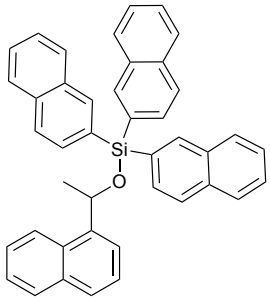
Triphenyl(1-(naphthalen-1-yl)ethoxy)silane **5bd**



5bd

Synthesized according to GP4 using **1b** and **2d** yielding in a colourless oil (94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (1H, d, *J* = 8.1 Hz, Ar-*H*), 7.87 – 7.80 (2H, m, Ar-*H*), 7.74 (1H, d, *J* = 8.2 Hz, Ar-*H*), 7.64 (6H, d, *J* = 7.9 Hz, Ar-*H*), 7.51 – 7.38 (6H, m, Ar-*H*), 7.36 – 7.27 (6H, m, Ar-*H*), 5.80 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.60 (3H, d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.66 (s), 135.49, 134.50, 133.70 (s), 129.99, 129.80 (s), 128.78, 127.84, 127.42, 125.63, 125.58, 125.21, 123.39, 123.10, 69.61 (O-*C*H), 26.44 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -13.22. **HRMS** (70 eV, EI) m/z calc. $C_{30}H_{26}OSi$ for $[M]^+$ 430.1753; found 430.1746.

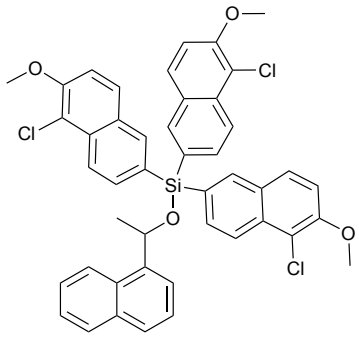
Tri(naphtalen-2-yl)(1-(naphthalen-1-yl)ethoxy)silane **5be**



5be

Synthesized according to GP4 using **1b** and **2e** yielding in a colourless oil (93%). **R_f** 0.60 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (3H, s, Ar-*H*), 8.01 (1H, d, *J* = 8.3 Hz, Ar-*H*), 7.92 – 7.81 (8H, m, Ar-*H*), 7.80 – 7.67 (7H, m, Ar-*H*) 7.53 (3H, t, *J* = 7.4 Hz, Ar-*H*), 7.50 – 7.40 (5H, m, Ar-*H*), 7.40 – 7.34 (1H, m, Ar-*H*), 5.95 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.72 (3H, d, *J* = 6.3, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.71(s), 137.17, 134.35 (s), 133.89 (s), 132.95 (s), 132.09 (s), 131.22, 130.05 (s), 128.88, 128.61, 127.85, 127.71, 127.29, 127.00, 126.08, 125.74, 125.67, 125.37, 123.64, 123.53, 70.32 (O-*C*H), 26.58 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.71. **HRMS** (70 eV, EI) m/z calc. for $C_{42}H_{32}OSi$ $[M]^+$ 580.2222; found 580.2225.

Tris(5-chloro-6-methoxynaphthalen-2-yl)(1-(naphthalen-1-yl)ethoxy)silane **5bf**

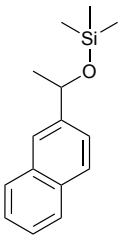


5bf

Synthesized according to GP4 using **1b** and **2f** yielding in a colourless oil (81%). **R_f** 0.72 (*i*Hex:EtOAc=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (3H, d, *J* = 8.5 Hz, Ar-*H*), 8.06 (3H, s, Ar-*H*), 7.98 (1H, d, *J* = 8.5 Hz, Ar-*H*), 7.84 – 7.79 (5H, m, Ar-*H*), 7.72 (1H, d, *J* = 8.2 Hz, Ar-*H*), 7.60 (3H, d, J = 9.0 Hz, Ar-*H*), 7.45 – 7.31 (3H, m, Ar-*H*), 7.24 (2H, d, J = 1.9 Hz, Ar-*H*), 5.89 (1H, q, *J* = 6.3 Hz, C*H*-CH_3), 4.02 (9H, s, O-CH_3), 1.71 (3H, d,

J = 6.4 Hz, CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.33 (s), 141.36 (s), 137.09, 133.74 (s), 132.72 (s), 132.53, 129.86 (s), 129.81 (s), 128.91 (s), 128.74, 128.65, 127.67, 125.64, 125.47, 125.26, 123.41, 123.39, 122.77, 116.69 (s), 113.52, 70.27 (O-*C*H), 56.88 (O-*C*H$_3$), 26.37 (O-CH-*C*H$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.82. **HRMS** (70 eV, EI) m/z calc. for $C_{45}H_{35}Cl_3O_4Si$ $[M]^+$ 772.1370; found 772.1365.

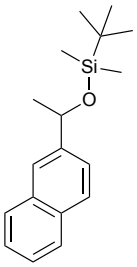
Trimethyl(1-(naphthalen-2-yl)ethoxy)silane **5ca**[47]



5ca

Synthesized according to GP4 using **1c** and **2a** yielding in a colourless oil (94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (3H, m, Ar-*H*), 7.78 (1H, s, Ar-*H*), 7.55 – 7.41 (3H, m, Ar-*H*), 5.05 (1H, q, *J* = 6.4 Hz, O-C*H*-CH$_3$), 1.54 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$), 0.13 (9H, s, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.97 (s), 133.33 (s), 132.74 (s), 127.92 (2C), 127.66, 125.93, 125.49, 124.12, 123.64, 70.80 (O-*C*H), 26.92 (O-CH-*C*H$_3$), 0.18 (Si-*C*H$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -17.00. **HRMS** (70 eV, EI) m/z calc. for $C_{15}H_{20}OSi$ $[M]^+$ 244.1283; found 244.1276.

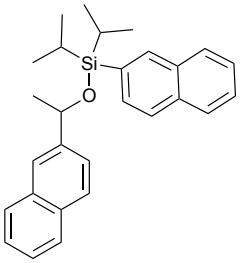
tert-Butyldimethyl (1-(naphthalen-2-yl)ethoxy)silane **5cb**



5cb

Synthesized according to GP4 using **1c** and **2b** yielding in a colourless oil (93%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (3H, m, Ar-*H*), 7.81 (1H, s, Ar-*H*), 7.61 – 7.46 (3H, m, Ar-*H*), 5.08 (1H, q, *J* = 6.4 Hz, O-C*H*-CH$_3$), 1.54 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$), 0.98 (9H, s, Si-C-C*H*$_3$), 0.13 (3H, s, Si-C*H*$_3$), 0.05 (3H, s, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.46 (s), 133.37 (s), 132.71 (s), 127.95, 127.86, 127.70, 125.91, 125.43, 124.07, 123.48, 71.05 (O-*C*H), 27.30 (Si-*C*-CH$_3$), 25.96 (Si-C-*C*H$_3$), 18.38 (O-CH-*C*H$_3$), -4.68 (Si-*C*H$_3$), -4.74 (Si-*C*H$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 18.98. **HRMS** (70 eV, EI) m/z calc. for $C_{18}H_{26}OSi$ $[M]^+$ 286.1753; found 286.1745.

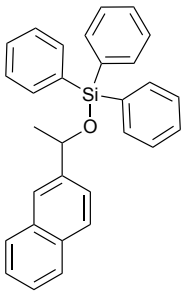
Diisopropyl(naphtalen-2-yl)(1-(naphthalen-2-yl)ethoxy)silane **5cc**



5cc

Synthesized according to GP4 using **1c** and **2c** yielding in a colourless oil (78%). $\mathbf{R_f}$ 0.78 (iHex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (1H, s, Ar-*H*), 7.90 – 7.79 (6H, m, Ar-*H*), 7.74 (1H, d, J = 7.5 Hz, Ar-*H*), 7.65 – 7.59 (2H, m, Ar-*H*), 7.53 – 7.44 (4H, m, Ar-*H*), 5.24 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.64 (3H, d, *J* = 6.2 Hz, O-CH-CH_3), 1.42 (2H, heptd, *J* = 7.4, 1.6 Hz, iPr-C*H*), 1.12 – 1.01 (12H, m, iPr-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.53 (s), 135.94, 133.98 (s), 133.47 (s), 132.93 (s), 132.91 (s), 132.43 (s), 131.05, 128.39, 128.13, 128.08, 127.84, 127.78, 126.73, 126.49, 126.05, 125.83, 125.61, 124.22, 123.88, 72.03 (O-*C*H), 27.87 (O-CH-*C*H_3), 17.66 (iPr-*C*H_3), 17.62 (iPr-*C*H_3), 17.56 (iPr-*C*H_3), 17.47 (iPr-*C*H_3), 12.64 (iPr-*C*H), 12.55 (iPr-*C*H). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 6.91. **HRMS** (70 eV, EI) m/z calc. for $C_{28}H_{32}OSi$ $[M]^+$ 412.2222; found 412.2197.

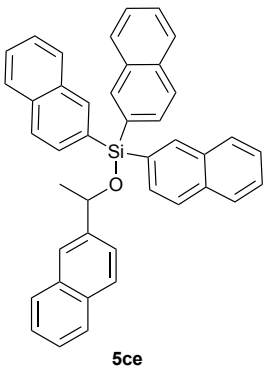
Triphenyl*(1-(naphthalen-2-yl)ethoxy)silane* **5cd**[46]



5cd

Synthesized according to GP4 using **1c** and **2e** yielding in a colourless oil (94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (3H, m, Ar-*H*), 7.74 (1H, s, Ar-*H*), 7.72 – 7.65 (6H, m, Ar-H), 7.57 (1H, dd, *J* = 8.5, 1.7 Hz, Ar-*H*), 7.51 – 7.41 (6H, m, Ar-*H*), 7.41 – 7.34 (6H, m, Ar-*H*), 5.26 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.56 (d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.44 (s), 135.62, 135.12 (s), 134.66 (s), 133.39 (s), 132.85 (s), 130.08, 128.10, 128.03, 127.92, 127.74, 125.96, 125.60, 124.23, 124.11, 72.32 (O-*C*H), 26.93 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.94. **HRMS** (70 eV, EI) m/z calc. for $C_{30}H_{26}OSi$ $[M]^+$ 430.1753; found 430.1748.

Tri(naphtalen-2-yl)(1-(naphthalen-2-yl)ethoxy)silane **5ce**

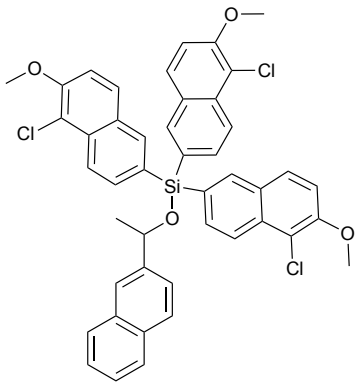


5ce

Synthesized according to GP4 using **1c** and **2e** yielding in a colourless oil (81%). $\mathbf{R_f}$ 0.63 (iHex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (3H, s, Ar-*H*), 7.88 – 7.81 (8H, m, Ar-*H*), 7.80 – 7.69 (8H, m, Ar-*H*), 7.62 (1H, dd, J = 8.5, 1.7 Hz, Ar-*H*), 7.56 – 7.43 (8H, m, Ar-*H*), 5.37 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.64 (3H, d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.37 (s), 137.19, 134.36

(s), 133.40 (s), 132.97 (s), 132.94 (s), 132.14 (s), 131.25, 128.61, 128.15, 128.08, 127.87, 127.74, 127.30, 127.02, 126.11, 126.03, 125.68, 124.38, 124.35, 72.76 (O-*C*H), 26.95 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.93. **HRMS** (70 eV, EI) m/z calc. for $C_{42}H_{32}OSi$ $[M]^+$ 580.2222; found 580.2222.

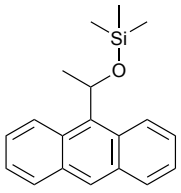
Tris(5-chloro-6-methoxynaphthalen-2-yl)(1-(naphthalen-2-yl)ethoxy)silane **5cf**



5cf

Synthesized according to GP4 using **1c** and **2f** yielding in a colourless oil (81%). **R_f** 0.72 (*i*Hex:EtOAc=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (3H, d, *J* = 8.5 H, Ar-*H*), 8.05 (3H, s, Ar-*H*), 7.86 – 7.75 (6H, m, Ar-*H*), 7.67 – 7.63 (2H, m, Ar-*H*), 7.61 (3H, d, *J* = 9.0 Hz, Ar-*H*), 7.56 (1H, dd, *J* = 8.5, 1.6 Hz, Ar-*H*), 7.46 – 7.38 (2H, m, Ar-*H*), 7.24 (2H, d, *J* = 4.1 Hz, Ar-*H*), 5.29 (1H, q, *J* = 6.3 Hz, C*H*-CH_3), 4.02 (9H, s, O-CH_3), 1.61 (3H, d, *J* = 6.4 Hz, CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.32 (s), 142.94 (s), 137.08, 133.17 (s), 132.78 (s), 132.72 (s), 132.54, 129.86 (s), 128.91 (s), 128.62, 128.05, 127.83, 127.55, 125.91, 125.58, 124.27, 124.08, 122.76, 116.70 (s), 113.53, 72.73 (O-*C*H), 56.88 (O-*C*H_3), 26.70 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.12. **HRMS** (70 eV, EI) m/z calc. for $C_{45}H_{35}Cl_3O_4Si$ $[M]^+$ 772.1370; found 772.1365.

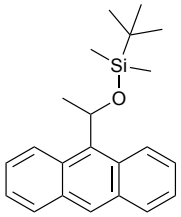
(1-(Anthracen-9-yl)ethoxy)trimethylsilane **5da**



5da

Synthesized according to GP4 using **1d** and **2a** yielding in a yellow oil (95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (2H, br-s, Ar-*H*), 8.42 (1H, s, Ar-*H*), 8.04 (2H, d, *J* = 8.2 Hz, Ar-*H*), 7.58 – 7.47 (4H, m, Ar-*H*), 6.48 (1H, q, *J* = 6.6 Hz, O-C*H*-CH_3), 1.95 (3H, d, *J* = 6.7 Hz, O-CH-CH_3), -0.01 (9H, s, Si-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.82 (s), 131.86 (s), 129.37, 127.61 (2C), 125.26 (s), 124.76 (2C), 67.54 (O-*C*H), 25.49 (O-CH-*C*H_3), -0.08 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 17.50. **HRMS** (70 eV, EI) m/z calc. for $C_{19}H_{22}OSi$ $[M]^+$ 294.1440; found 294.1434.

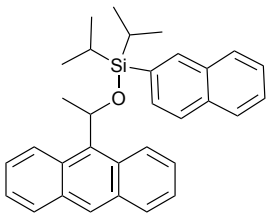
(1-(Anthracen-9-yl)ethoxy)tert-butyldimethylsilane **5db**



5db

Synthesized according to GP4 using **1d** and **2b** yielding in a yellow solid (79%). **mp** 85 – 87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.20 (1H, br-s, Ar-*H*), 8.38 (1H, s, Ar-*H*), 8.25 (1H, br-s, Ar-*H*), 8.00 (2H d, *J* = 9.3 Hz, Ar-*H*), 7.57 – 7.38 (4H, m, Ar-*H*), 6.40 (1H, q, *J* = 6.6 Hz, O-C*H*-CH_3), 1.87 (3H, d, *J* = 6.8 Hz, O-CH-CH_3), 0.87 (9H, s, Si-C-CH_3), 0.03 (3H, s, Si-CH_3), -0.36 (3H, s, Si-CH_3). **^{13}C NMR**[1] (101 MHz, $CDCl_3$) δ 136.97, 129.26, 127.42, 124.69, 67.78 (O-*C*H), 25.96 (Si-C-*C*H_3), 25.48 (O-CH-*C*H_3), 18.30 (s, Si-C-*C*H_3), -4.89 (Si-*C*H_3), -4.93 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 18.92. **HRMS** (70 eV, EI) m/z calc. for $C_{22}H_{28}OSi$ $[M]^+$ 336.1909; found 336.1902.

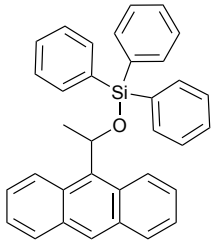
(1-(Anthracen-9-yl)ethoxy)diisopropyl(naphtalen-2-yl)silane **5dc**



5dc

Synthesized according to GP4 using **1d** and **2c** yielding in a yellow oil (76%). **R_f** 0.71 (*i*Hex:EtOAc=19:1) . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (1H, br-s, Ar-*H*), 8.40 (1H, s, Ar-*H*), 8.07 – 7.94 (3H, d, *J* = 6.2 Hz, Ar-*H*), 7.87 (1H, s, Ar-*H*), 7.77 (1H, d, *J* = 8.0 Hz, Ar-*H*), 7.69 (1H, d, *J* = 8.1 Hz, Ar-*H*), 7.55 – 7.34 (8H, m, Ar-*H*), 6.57 (1H, q, *J* = 6.7 Hz, O-C*H*-CH_3), 2.01 (3H, d, *J* = 6.7 Hz, O-CH-CH_3), 1.45 – 1.26 (2H, m, Si-C*H*), 0.98 (6H, t, *J* = 7.6 Hz, Si-CH-CH_3), 0.86 (6H, dd, *J* = 19.5, 7.4 Hz, Si-CH-CH_3). **^{13}C NMR**[1] (101 MHz, $CDCl_3$) δ 136.85, 136.04, 134.28 (s), 133.84, 132.79, 132.01, 130.87, 128.72 (s), 128.32, 127.65, 127.63, 127.38 (s), 126.60, 126.40, 126.13 (s), 125.68, 125.48 (s), 125.24 (s), 68.47 (O-*C*H), 25.55 (O-CH-*C*H_3), 17.58 (*i*Pr-*C*H_3), 17.45 (*i*Pr-*C*H_3), 17.25 (*i*Pr-*C*H_3), 12.38 (*i*Pr-*C*H). **HRMS** (70 eV, EI) m/z calc. for $C_{32}H_{34}OSi$ $[M]^+$ 462.2379; found 462.2374.

(1-(Anthracen-9-yl)ethoxy)triphenylsilane **5dd**



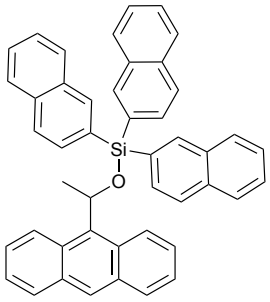
5dd

Synthesized according to GP4 using **1d** and **2d** yielding in a colourless oil (96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (1H, br-s, Ar-*H*), 8.32 (1H, s, Ar-*H*), 7.96 (2H, d, *J* = 7.8 Hz, Ar-*H*), 7.70 (1H, d, *J* = 6.7 Hz, Ar-*H*), 7.52 (6H, d, *J* = 6.9 Hz, Ar-*H*), 7.45 – 7.37 (3H, m, Ar-*H*), 7.36 – 7.31 (3H, m, Ar-*H*), 7.29 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.27 – 7.20 (6H, m, Ar-*H*),

[1] In all of the ^{13}C-NMR spectra of silylethers with alcohol **1d** the resolution of the alcohol carbons is diffuse due to intramolecular interactions.

6.54 (1H, q, *J* = 6.7 Hz, O-C*H*-CH_3), 1.92 (3H, d, J = 6.7 Hz, O-CH-CH_3). **^{13}C NMR**[1] (101 MHz, $CDCl_3$) δ 135.94, 135.59, 135.46, 135.32, 134.32, 129.93, 129.17, 127.84, 127.79, 127.68, 68.81 (O-*C*H), 25.16 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.40. **HRMS** (70 eV, EI) m/z calc. for $C_{34}H_{28}OSi$ $[M]^+$ 480.1909; found 480.1904.

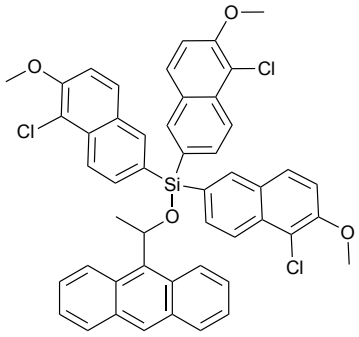
(1-(Anthracen-9-yl)ethoxy)tri(naphtalen-2-yl)silane **5de**



5de

Synthesized according to GP4 using **1d** and **2e** yielding in a yellow solid (94%). **mp** 115 °C. **R_f** 0.60 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (1H, br-s, Ar-*H*), 8.27 (1H, s, Ar-*H*), 8.08 (3H, s, Ar-*H*), 7.90 (2H, s, Ar-*H*), 7.79 (3H, d, *J* = 8.1 Hz, Ar-*H*), 7.71 (3H, d, *J* = 8.2 Hz, Ar-*H*), 7.69 – 7.35 (10H, m, Ar-*H*), 7.63 (3H, d, *J* = 8.1 Hz, Ar-*H*), 7.57 (3H, d, *J* = 8.1 Hz, Ar-*H*), 7.01 (1H, br-s, Ar-*H),* 6.69 (1H, q, *J* = 6.7 Hz, O-C*H*-CH_3), 2.03 (3H, d, *J* = 6.7 Hz, O-CH-CH_3). **^{13}C NMR**[1] (101 MHz, $CDCl_3$) δ 137.05, 135.87 (s), 134.24 (s), 132.85 (s), 131.78 (s), 130.94, 129.19, 128.56 (s), 127.77, 127.27, 127.15, 127.02, 126.91, 126.06, 125.97, 124.70, 69.10 (O-*C*H), 25.22 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.02. **HRMS** (70 eV, EI) m/z calc. for $C_{46}H_{34}OSi$ $[M+H]^+$ 631.2457; found 631.2447.

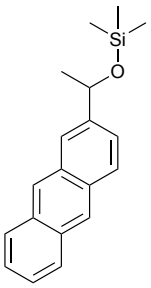
(1-(Anthracen-9-yl)ethoxy)tris(5-chloro-6-methoxynaphthalen-2-yl)silane **5df**



5df

Synthesized according to GP4 using **1d** and **2f** yielding in a yellow oil (72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (1H, br-s, Ar-*H*), 8.26 (1H, s, Ar-*H*), 8.24 – 8.14 (1H, br-s, Ar-*H*), 8.09 (3H, d, *J* = 8.5 Hz, Ar-*H*), 7.96 (3H, s, Ar-*H*), 7.95 – 7.71 (4H, m, Ar-*H*), 7.67- 7.31 (4H, m, Ar-*H*), 7.69 (3H, d, *J* = 9.4 Hz, Ar-*H*), 7.50 (3H, d, *J* = 9.0 Hz, Ar-*H*), 7.29 (5H, d, *J* = 4.0 Hz, Ar-*H*), 7.03 (1H, br-s, Ar-*H*), 6.66 (1H, q, *J* = 6.7 Hz, O-C*H*-CH_3), 4.07 (9H, s, O-CH_3), 2.07 (3H, d, *J* = 6.7 Hz, O-CH-CH_3). **^{13}C NMR**[1] (101 MHz, $CDCl_3$) δ 153.36, 137.07, 135.62, 134.28, 133.64, 132.73, 132.48, 129.60, 129.20, 128.94, 128.76, 127.83, 127.38, 122.75, 116.69, 113.50, 69.15 (O-CH), 57.04 (O-*C*H_3), 29.86 (grease), 25.15 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.84. **HRMS** (70 eV, EI) m/z calc. for $C_{49}H_{37}Cl_3O_4Si$ $[M]^+$ 822.1527; found 822.1531.

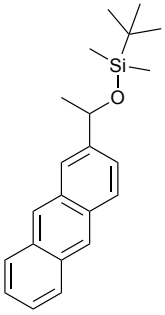
(1-(anthracen-2-yl)ethoxy)trimethylsilane **5ea**



5ea

Synthesized according to GP4 using **1e** and **2a** yielding in a brown solid (99%). **mp** 123 – 125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (2H, s, Ar-*H*), 8.03 – 7.93 (3H, m, Ar-*H*), 7.91 (1H, s, Ar-*H*), 7.52 – 7.40 (3H, m, Ar-*H*), 5.06 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.56 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$), 0.13 (9H, s, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.16 (s), 131.82 (s), 131.55 (s), 131.52 (s), 131.16 (s), 128.22, 128.12, 128.02, 126.06, 125.92, 125.24, 125.09, 124.09, 123.33, 70.84 (O-*C*H), 26.44 (O-CH-*C*H_3), 0.15 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -17.59. **HRMS** (70 eV, EI) m/z calc. for $C_{19}H_{22}OSi$ $[M]^+$ 294.1440; found 294.1436.

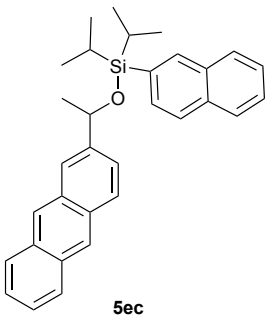
(1-(anthracen-2-yl)ethoxy)tert-butyldimethyl silane **5eb**



5eb

Synthesized according to GP4 using **1e** and **2b** yielding in a colourless oil (83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (1H, s, Ar-*H*), 8.44 (1H, s, Ar-*H*), 8.11 – 8.00 (3H, m, Ar-*H*), 7.52 (1H, s, Ar-*H*), 7.60 – 7.42 (3H, m, Ar-*H*), 5.13 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.60 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$), 1.04 (9H, s, Si-C-C*H*$_3$), 0.19 (3H, s, Si-C*H*$_3$), 0.10 (3H, s, Si-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.72 (s), 131.93 (s), 131.69 (s), 131.60 (s), 131.25 (s), 128.25, 128.24, 128.12, 126.14, 126.05, 125.34, 125.16, 124.17, 123.23, 71.19 (O-*C*H), 26.93 (O-CH-*C*H_3), 26.03 (Si-C-*C*H_3), 18.44 (s, Si-*C*-CH_3), -4.61 (Si-*C*H_3), -4.67 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 19.08. **HRMS** (70 eV, EI) m/z calc. for $C_{22}H_{28}OSi$ $[M]^+$ 336.1909; found 336.1899.

(1-(anthracen-2-yl)ethoxy)diisopropyl(naphtalen-2-yl)silane **5ec**

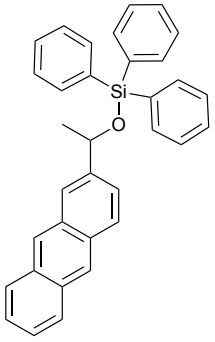


5ec

Synthesized according to GP4 using **1e** and **2c** yielding in a yellow oil (72%). **R_f** 0.63 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (1H, s, Ar-*H*), 8.40 (1H, s, Ar-*H*), 8.08 (1H, s, Ar-*H*), 8.07 – 7.99 (3H, m, Ar-*H*), 7.97 (1H, s, Ar-*H*), 7.86 – 7.79 (2H, m, Ar-*H*), 7.74 (1H, d, *J* = 8.0 Hz, Ar-*H*), 7.63 (2H, m, Ar-*H*), 7.52 – 7.43 (4H, m, Ar-*H*), 5.27 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.68 (3H, d, *J* = 6.3 Hz, O-CH-C*H*$_3$), 1.44 (2H, hept, *J* = 7.4 Hz, iPr-*C*H), 1.09 (12H, m, iPr-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.74 (s), 135.94, 133.98 (s), 132.91 (s), 132.43 (s), 132.00 (s), 131.71, 131.40

(s), 131.06, 128.50, 128.39, 128.32, 128.21, 127.77, 126.75, 126.49, 126.26, 126.16, 125.83, 125.43, 125.28, 124.24, 123.66, 72.12 (O-*C*H), 27.46 (O-CH-*C*H_3), 17.68 (iPr-*C*H_3), 17.63 (iPr-*C*H_3), 17.59 (iPr-*C*H_3), 17.49 (iPr-*C*H_3), 12.67 (iPr-*C*H), 12.57 (iPr-*C*H). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 6.96. **HRMS** (70 eV, EI) m/z calc. for $C_{32}H_{34}OSi$ $[M]^+$ 462.2379; found 462.2379.

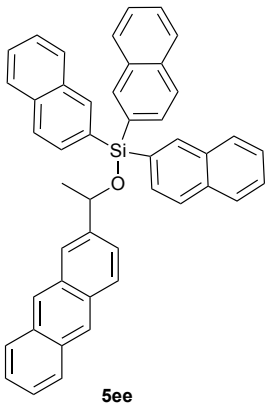
(1-(anthracen-2-yl)ethoxy)triphenylsilane **5ed**



5ed

Synthesized according to GP4 using **1e** and **2d** yielding in a colourless oil (94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (1H, s, Ar-*H*), 8.36 (1H, s, Ar-*H*), 8.08 – 7.96 (3H, m, Ar-*H*), 7.87 (1H, s, Ar-*H*), 7.76 – 7.68 (6H, m, Ar-*H*), 7.57 (1H, dd, *J* = 8.8, 1.6 Hz, Ar-*H*), 7.52 – 7.44 (5H, m, Ar-*H*), 7.42 – 7.37 (6H, m, Ar-*H*), 5.30 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.62 (3H, d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.67 (s), 135.63 , 135.13 (s), 134.66 (s)[2], 131.93 (s), 131.68 (s), 131.65 (s), 131.32 (s), 130.10, 128.40, 128.30, 128.21, 127.94, 126.33, 126.06, 125.38, 125.27, 124.22, 123.88, 72.42 (O-*C*H), 26.58 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.86. **HRMS** (70 eV, EI) m/z calc. for $C_{34}H_{28}OSi$ $[M]^+$ 480.1909; found 480.1899.

(1-(anthracen-2-yl)ethoxy)tri(naphtalen-2-yl)silane **5ee**



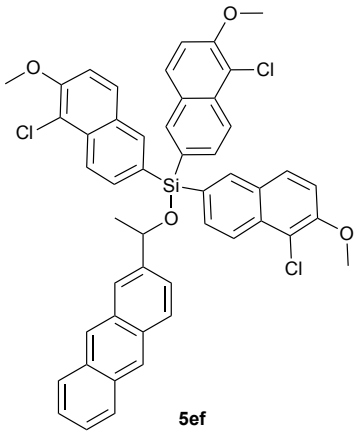
5ee

Synthesized according to GP4 using **1e** and **2e** yielding in a yellow oil (79%). **R_f** 0.52 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (1H, s, Ar-*H*), 8.23 (3H, s, Ar-*H*), 8.19 (1H, s, Ar-*H*), 8.03 – 7.92 (3H, m, Ar-*H*), 7.86 – 7.71 (13H, m, Ar-*H*), 7.61 (1H, dd, *J* = 8.8, 1.6 Hz, Ar-*H*), 7.56 – 7.49 (3H, m, Ar-*H*), 7.49 – 7.42 (5H, m, Ar-*H*), 5.38 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.67 (3H, d, *J* = 6.4 Hz, O-CH-C*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.50 (s), 137.19, 134.37, 132.97, 132.13 (s), 131.93 (s), 131.72 (s), 131.58 (s), 131.34 (s), 131.25, 128.61, 128.51, 128.28, 128.26, 127.86, 127.31, 127.02, 126.36, 126.10, 126.05, 125.34, 125.28, 124.28, 124.25, 72.87 (O-*C*H), 26.55 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz,

[2] Due to intramolecular interactions the C1-atom of the phenyl rest are not equivalent.

$CDCl_3$) δ -11.96. **HRMS** (70 eV, EI) m/z calc. for $C_{46}H_{34}OSi$ $[M]^+$ 630.2379; found 630.2378.

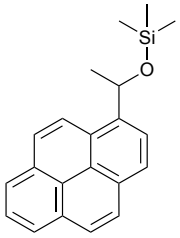
(1-(anthracen-2-yl)ethoxy)tris(5-chloro-6-methoxynaphthalen-2-yl)silane **5ef**



5ef

Synthesized according to GP4 using **1e** and **2f** yielding in a yellow solid (98%). **mp** 158 °C. $\mathbf{R_f}$ 0.72 (*i*Hex:EtOAc=1:1) . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (1H, s, Ar-*H*), 8.23 (3H, d, *J* = 8.5 Hz, Ar-*H*), 8.09 (4H, s, Ar-*H*), 8.00 – 7.90 (3H, m, Ar-*H*), 7.87 (3H, d, *J* = 8.6 Hz, Ar-*H*), 7.64 (1H, s, Ar-*H*), 7.59 (4H, d, *J* = 9.1 Hz, Ar-*H*), 7.49 – 7.42 (2H, m, Ar-*H*), 7.18 (3H, d, *J* = 9.0 Hz, Ar-*H*), 5.34 (1H, q, *J* = 6.3 Hz, C*H*-CH_3), 3.99 (9H, s, O-CH_3), 1.70 (3H, d, *J* = 6.4 Hz, CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.44, 142.08 (s), 137.25, 132.88, 132.68, 131.90 (s), 131.71 (s), 131.40 (s), 131.26 (s), 129.98 (s), 129.05, 128.75, 128.58 (s), 128.23 (s), 128.22 (s), 126.26 (s), 125.95 (s), 125.32 (s), 125.28 (s), 124.37, 124.08, 122.93, 116.78, 113.58, 73.08 (O-*C*H), 56.95 (O-*C*H_3), 26.43 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.29. **HRMS** (70 eV, EI) m/z calc. for $C_{49}H_{37}Cl_3O_4Si$ $[M]^+$ 822.1527; found 822.1516.

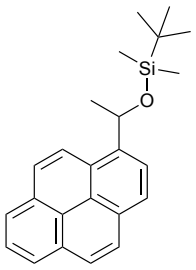
Trimethyl(1-(pyren-1-yl)ethoxy)silane **5fa**



5fa

Synthesized according to GP4 using **1f** and **2a** yielding in a colourless oil (97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (1H, d, *J* = 9.3 Hz, Ar-*H*), 8.36 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.26 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.23 – 8.19 (2H, m, Ar-*H*), 8.16 (1H, d, *J* = 9.3 Hz, Ar-*H*), 8.12 – 8.00 (3H, m, Ar-*H*), 6.01 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.82 (3H, d, *J* = 6.5 Hz, O-CH-CH_3), 0.21 (9H, s, Si-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.39 (s), 131.50 (s), 130.76 (s), 130.40 (s), 127.63, 127.36, 126.93, 126.74 (s), 125.84, 125.17, 125.15 (s), 125.14, 124.92 (s), 124.89, 123.59, 122.71, 68.39 (O-*C*H), 27.24 (O-CH-*C*H_3), 0.28 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 17.75. **HRMS** (70 eV, EI) m/z calc. for $C_{21}H_{22}OSi$ $[M]^+$ 318.1440; found 318.1438.

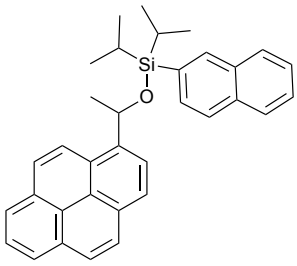
tert-Butyldimethyl(1-(pyren-1-yl)ethoxy)silane **5fb**



5fb

Synthesized according to GP4 using **1f** and **2b** yielding in a white solid (94%). **mp** 79-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (1H, d, *J* = 9.3 Hz, Ar-*H*), 8.31 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.26 – 8.17 (3H, m, Ar-*H*), 8.13 (1H, d, *J* = 9.3 Hz, Ar-*H*), 8.11 – 7.98 (3H, m, Ar-*H*), 5.95 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.73 (3H, d, *J* = 6.4 Hz, O-CH-CH_3), 0.99 (9H, s, Si-C-CH_3), 0.14 (3H, s, Si-CH_3), 0.01 (3H, s, Si-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.78 (s), 131.55 (s), 130.81 (s), 130.34 (s), 127.72, 127.34, 126.93, 126.66 (s), 125.90, 125.22, 125.20 (s), 125.16, 124.93 (2C), 123.59, 122.87, 68.82 (O-*C*H), 27.42 (O-CH-*C*H_3), 26.08 (Si-C-*C*H_3), 18.51 (Si-*C*-CH_3), -4.61 (Si-*C*H_3), -4.69 (Si-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 18.97. **HRMS** (70 eV, EI) m/z calc. for $C_{24}H_{28}OSi$ $[M]^+$ 360.1909; found 360.1904.

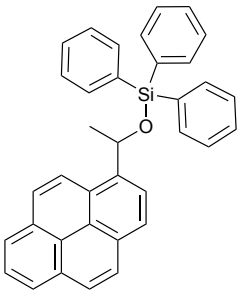
Diisopropyl(naphtalen-2-yl)(1-(pyren-1-yl)ethoxy)silane **5fc**



5fc

Synthesized according to GP4 using **1f** and **2c** yielding in white crystals (79%). **mp** 116 °C. **R_f** 0.77 (*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.31 (1H, d, *J* = 9.3 Hz, Ar-*H*), 8.26 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.22 – 8.15 (2H, m, Ar-*H*), 8.13 – 7.99 (5H, m, Ar-*H*), 7.84 – 7.76 (2H, m, Ar-*H*), 7.68 – 7.62 (2H, m, Ar-*H*), 7.51 – 7.39 (2H, m, Ar-*H*), 6.12 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.84 (3H, d, *J* = 6.4 Hz, O-CH-CH_3), 1.45 (2H, heptd, *J* = 7.5, 1.4 Hz, iPr-*C*H), 1.11 – 0.99 (12H, m, iPr-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.64 (s), 135.86, 133.89, 132.84, 132.24 (s), 131.50 (s), 130.93, 130.77 (s), 130.40 (s), 128.27, 127.67, 127.66, 127.34, 126.93, 126.72, 126.61 (s), 126.41, 125.83, 125.73, 125.21, 125.14 (s), 125.10, 124.89 (2C), 123.79 (s), 122.77 (s), 69.43 (O-*C*H), 27.65 (O-CH-*C*H_3), 17.59 (iPr-*C*H_3), 17.56 (iPr-*C*H_3), 17.50 (iPr-*C*H_3), 17.39 (iPr-*C*H_3), 12.63 (iPr-*C*H), 12.47 (iPr-*C*H). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ 7.57. **HRMS** (70 eV, EI) m/z calc. for $C_{34}H_{34}OSi$ $[M]^+$ 486.2379; found 486.2374.

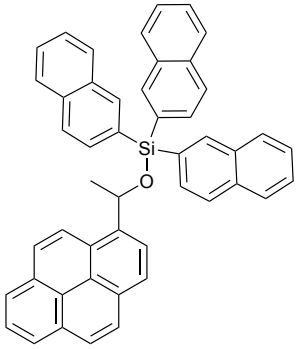
Triphenyl(1-(pyren-1-yl)ethoxy)silane **5fd**



5fd

Synthesized according to GP4 using **1f** and **2d** yielding in a colourless oil (96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (1h, d, *J* = 8.0 Hz, Ar-*H*), 8.17 (4H, dd, *J* = 19.2, 9.9 Hz, Ar-*H*), 8.07 (2H, s, Ar-*H*), 8.01 (2H, d, *J* = 9.4 Hz, Ar-*H*), 7.68 (6H, d, *J* = 6.7 Hz, Ar-*H*), 7.59 – 7.28 (9H, m, 9H), 6.14 (1H, q, *J* = 6.4 Hz, O-C*H*-CH_3), 1.74 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.64 (s), 135.43, 134.40, 131.35, 130.62, 130.28, 129.94, 127.80, 127.56, 127.10, 126.84, 126.55, 125.73, 125.12, 125.00, 124.96, 124.78, 124.70, 123.68, 122.69, 69.63 (O-*C*H), 26.97 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -12.41. **HRMS** (70 eV, EI) m/z calc. for $C_{36}H_{28}OSi$ $[M]^+$ 504.1909; found 504.1899.

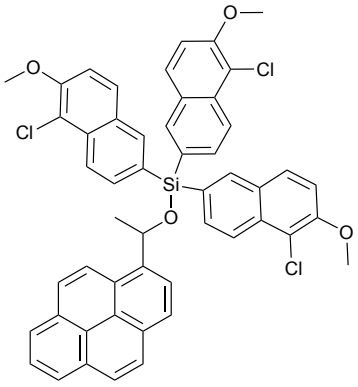
Tri(naphtalen-2-yl)(1-(pyren-1-yl)ethoxy)silane **5fe**



5fe

Synthesized according to GP4 using **1f** and **2e** yielding in a white solid (79%). **mp** 112 °C. **R_f** 0.50(*i*Hex:EtOAc=19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.19 (3H, s, Ar-*H*), 8.18 – 8.05 (5H, m, Ar-*H*), 8.03 (2H, s, Ar-*H*), 7.97 (1H, t, *J* = 7.6 Hz, Ar-*H*), 7.87 (1H, d, *J* = 9.3 Hz, Ar-*H*), 7.79 (3H, d, *J* = 8.0 Hz, Ar-*H*), 7.77 – 7.73 (5H, m, Ar-*H*), 7.65 (3H, d, *J* = 8.1 Hz, Ar-*H*), 7.53 – 7.44 (3H, m, Ar-*H*), 7.40 (3H, t, *J* = 8.0 Hz, Ar-*H*), 6.24 (1H, q, *J* = 6.3 Hz, O-C*H*-CH_3), 1.82 (3H, d, *J* = 6.4 Hz, O-CH-C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.66 (s), 137.13, 134.30, 132.90, 131.99, 131.49 (s), 131.15, 131.02 (s), 130.75 (s), 130.54 (s), 128.55, 127.79, 127.64, 127.30, 127.07, 126.96, 126.88 (s), 126.04, 125.84, 125.24, 125.12, 125.04 (s), 124.96, 124.83 (s), 124.08, 122.82, 70.18 (O-*C*H), 27.16 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.57. **HRMS** (70 eV, EI) m/z calc. for $C_{48}H_{234}OSi$ $[M]^+$ 654.2379; found 654.2390.

Tris(5-chloro-6-methoxynaphthalen-2-yl)(1-(pyren-1-yl)ethoxy)silane **5ff**



5ff

Synthesized according to GP4 using **1f** and **2f** yielding in a white solid (88%). **mp** 150 – 153 °C. $\mathbf{R_f}$ 0.70 (*i*Hex:EtOAc=1:1). **1H NMR** (400 MHz, $CDCl_3$) δ 8.37 (1H, d, *J* = 8.0 Hz, Ar-*H*), 8.16 – 8.10 (5H, m, Ar-*H*), 8.07 – 7.99 (7H, m, Ar-*H*), 7.95 (1H, t, *J* = 7.6 Hz, Ar-*H*), 7.85 – 7.80 (4H, m, Ar-*H*), 7.49 (3H, d, *J* = 9.0 Hz, Ar-*H*), 7.13 (3H, d, *J* = 9.1 Hz, Ar-*H*), 6.20 (1H, q, *J* = 6.3 Hz, O-C*H*), 3.99 (9H, s, O-CH_3), 1.88 (3H, d, *J* = 6.4 Hz, O-CH-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.32 (s), 139.36 (s), 137.11, 132.76 (s), 132.56, 131.43 (s), 130.62 (s), 130.52 (s), 129.78, 128.92 (s), 128.64, 127.52, 127.28, 127.11, 126.87 (s), 125.79, 125.18, 125.06, 124.89, 124.87, 124.64 (s), 124.10, 122.88, 122.55, 116.65 (s), 113.44, 70.11 (O-*C*H), 56.92 (O-*C*H_3), 27.04 (O-CH-*C*H_3). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -11.88. **HRMS** (70 eV, EI) m/z calc. for $C_{51}H_{37}Cl_3O_4Si$ $[M]^+$ 846.1527; found 846.1526.

5.3. NMR Spectra of Synthesized Products

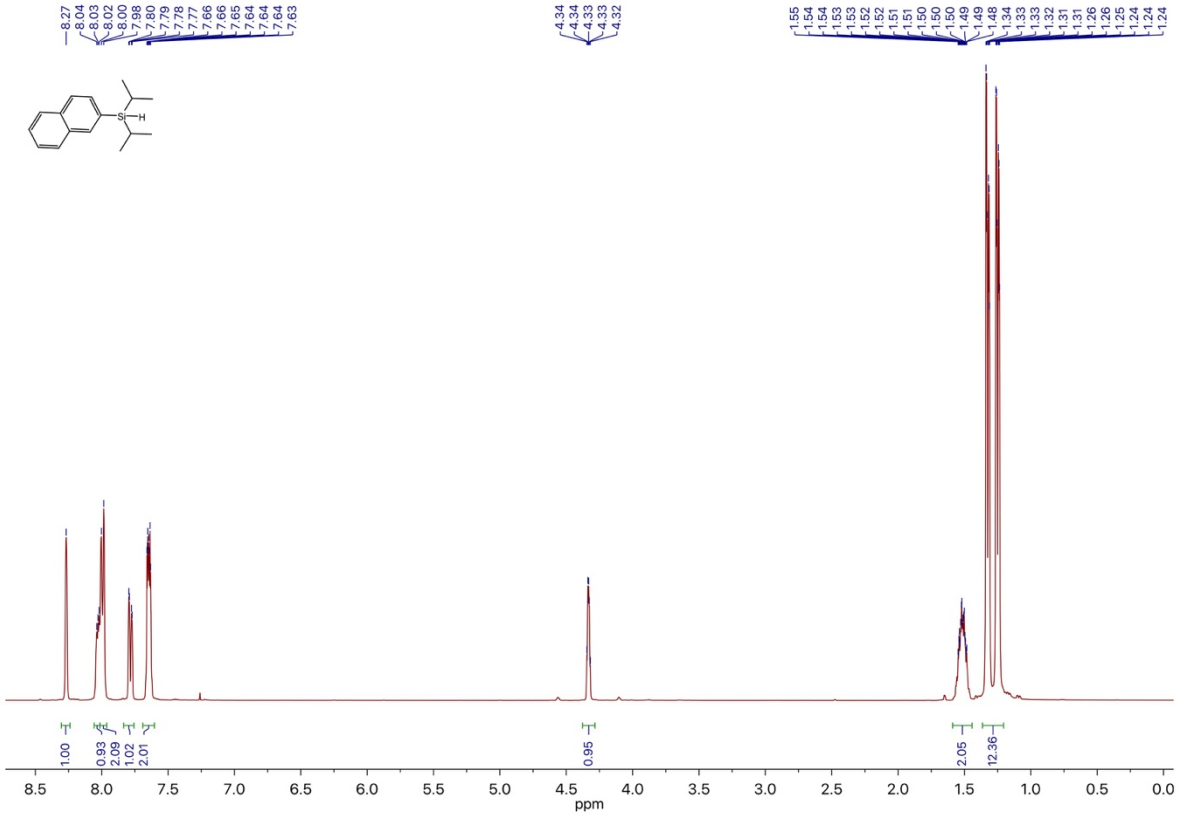


Figure S20: ^{1}H NMR spectrum of silane **7c** (400 MHz, $CDCl_3$).

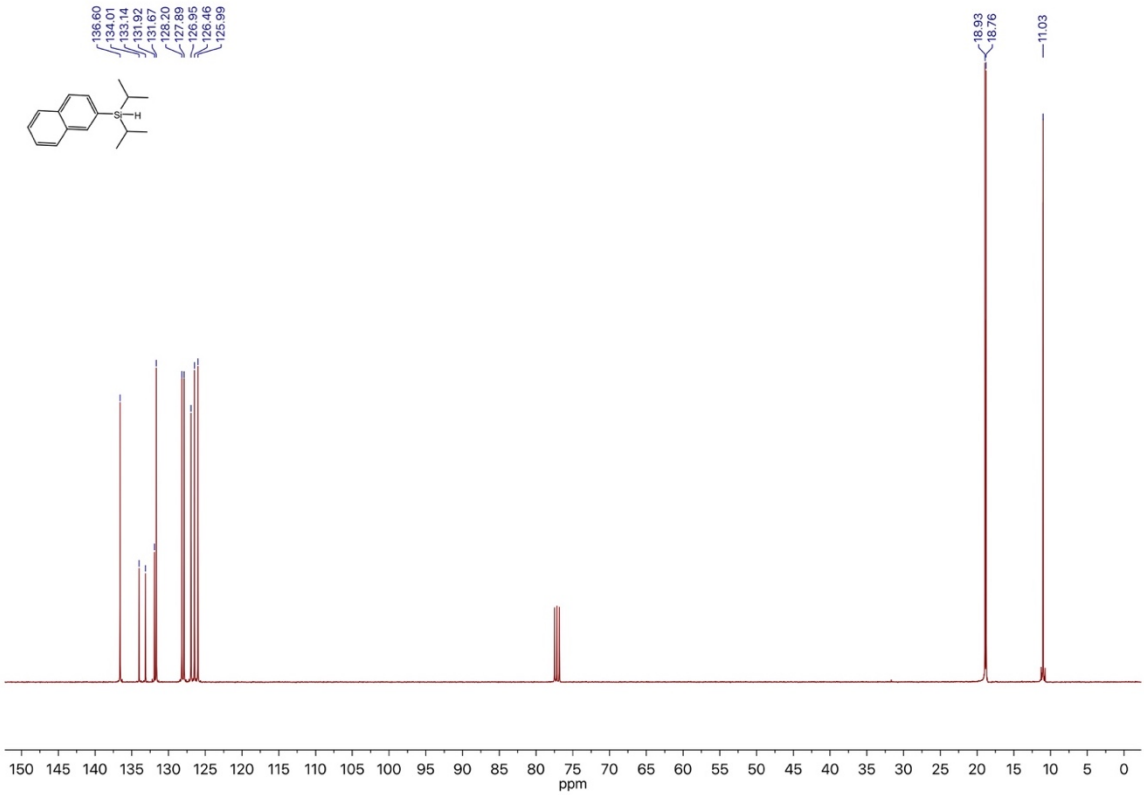


Figure S21: ^{13}C NMR spectrum of silane **7c** (101 MHz, $CDCl_3$).

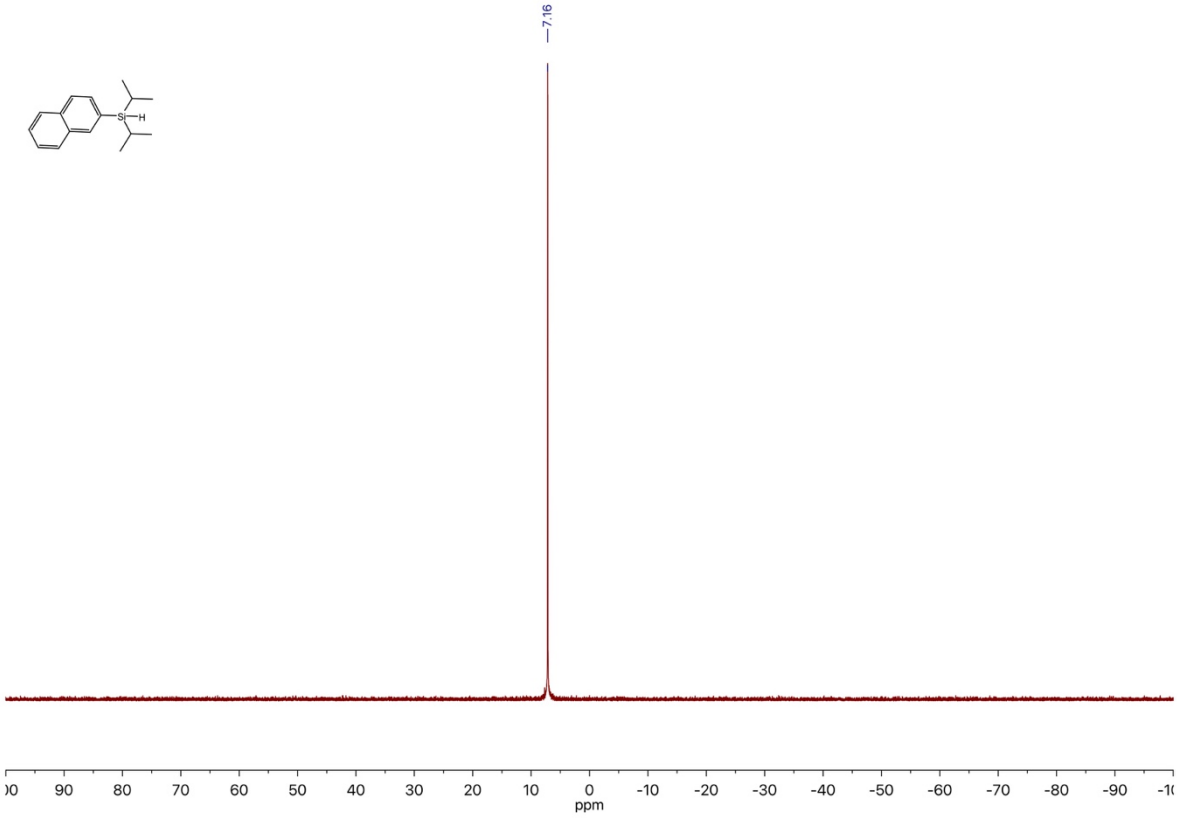


Figure S22: ^{29}Si NMR spectrum of silane **7c** (53.7 MHz, $CDCl_3$).

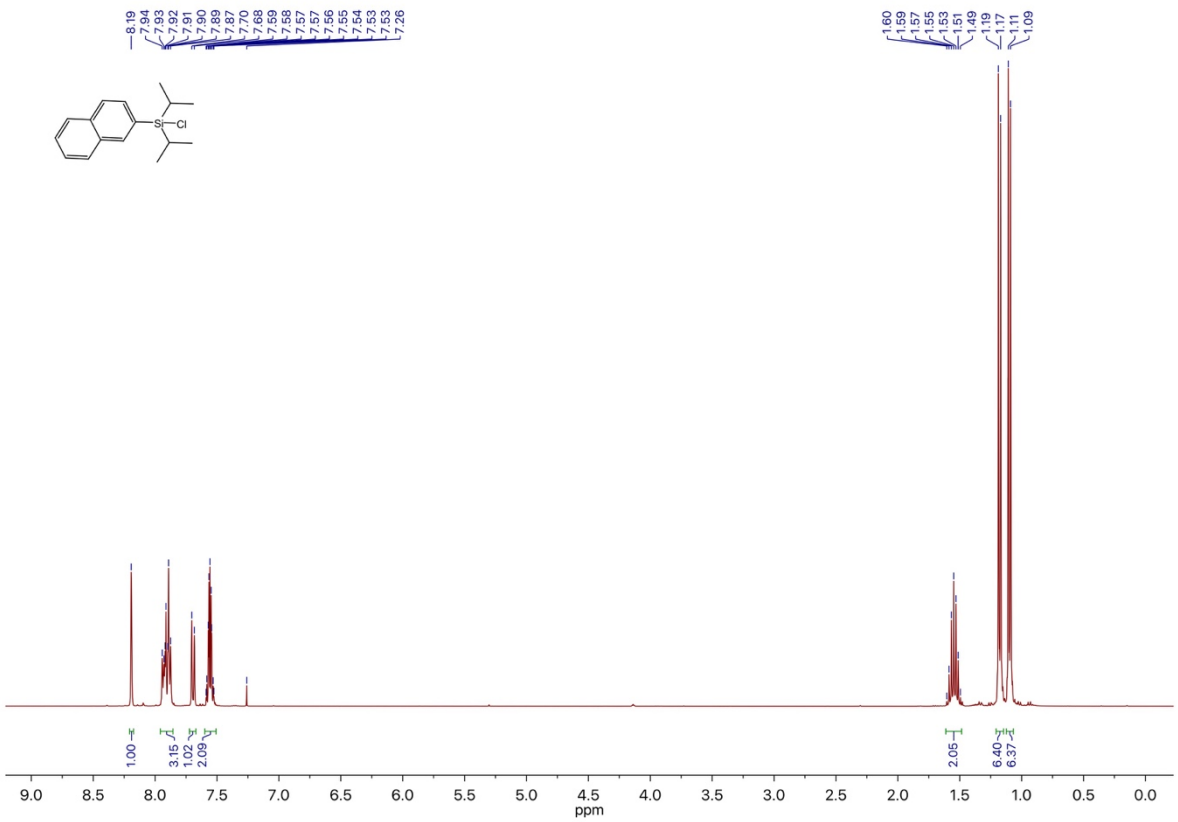


Figure S23: ^{1}H NMR spectrum of silyl chloride **2c** (400 MHz, $CDCl_3$).

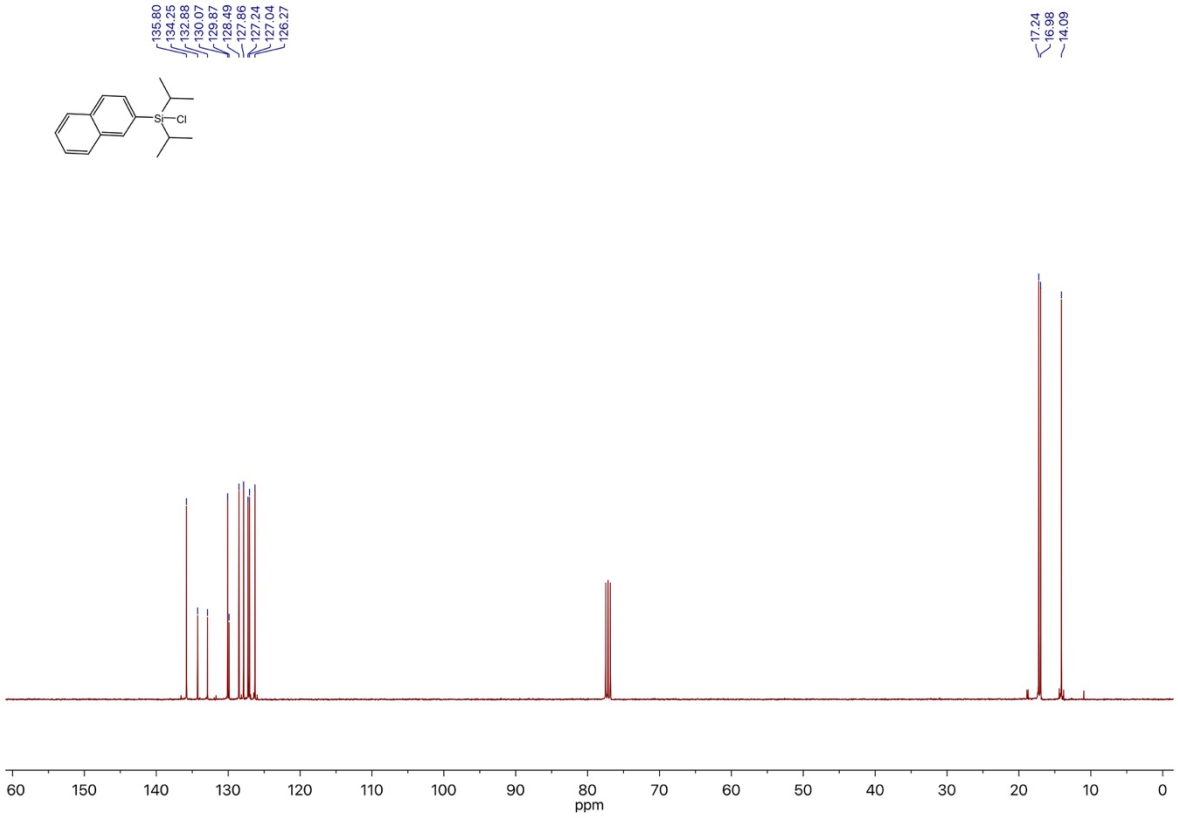


Figure S24: ^{13}C NMR spectrum of silyl chloride **2c** (101 MHz, $CDCl_3$).

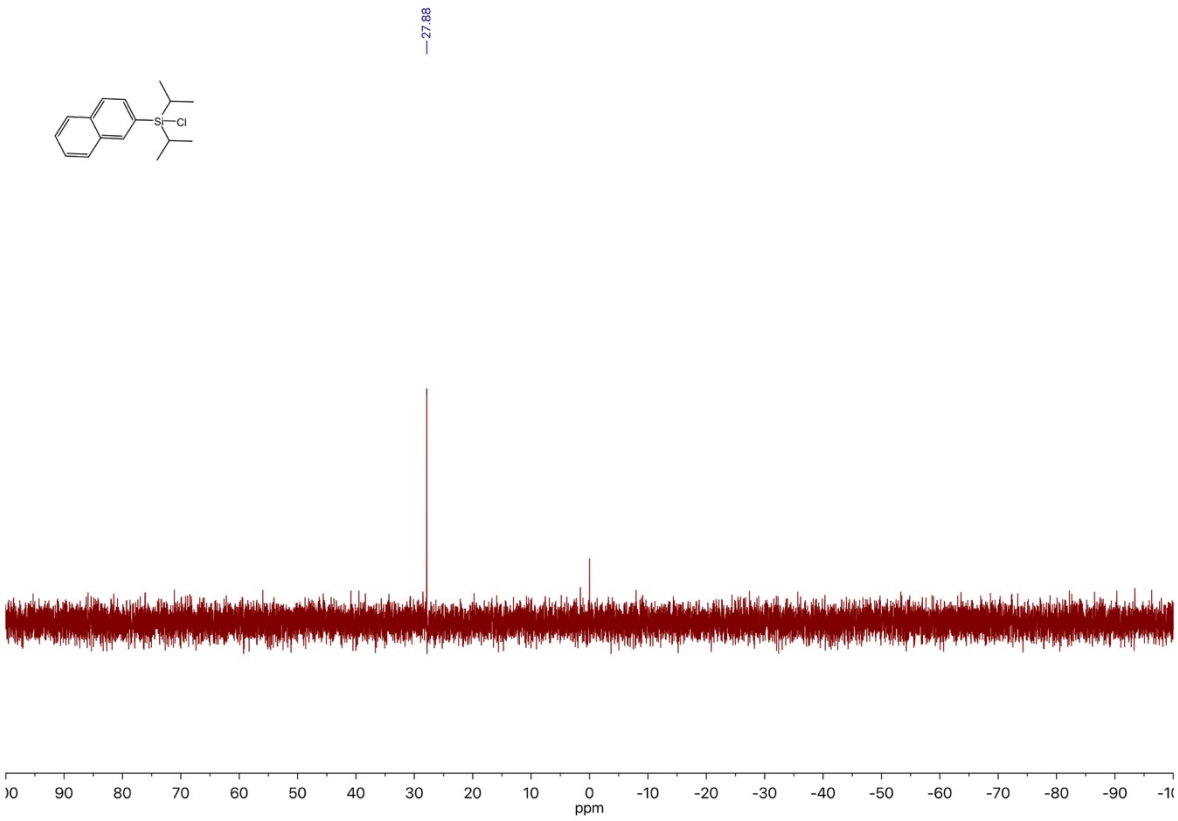


Figure S25: ^{29}Si NMR spectrum of silyl chloride **2c** (53.7 MHz, $CDCl_3$).

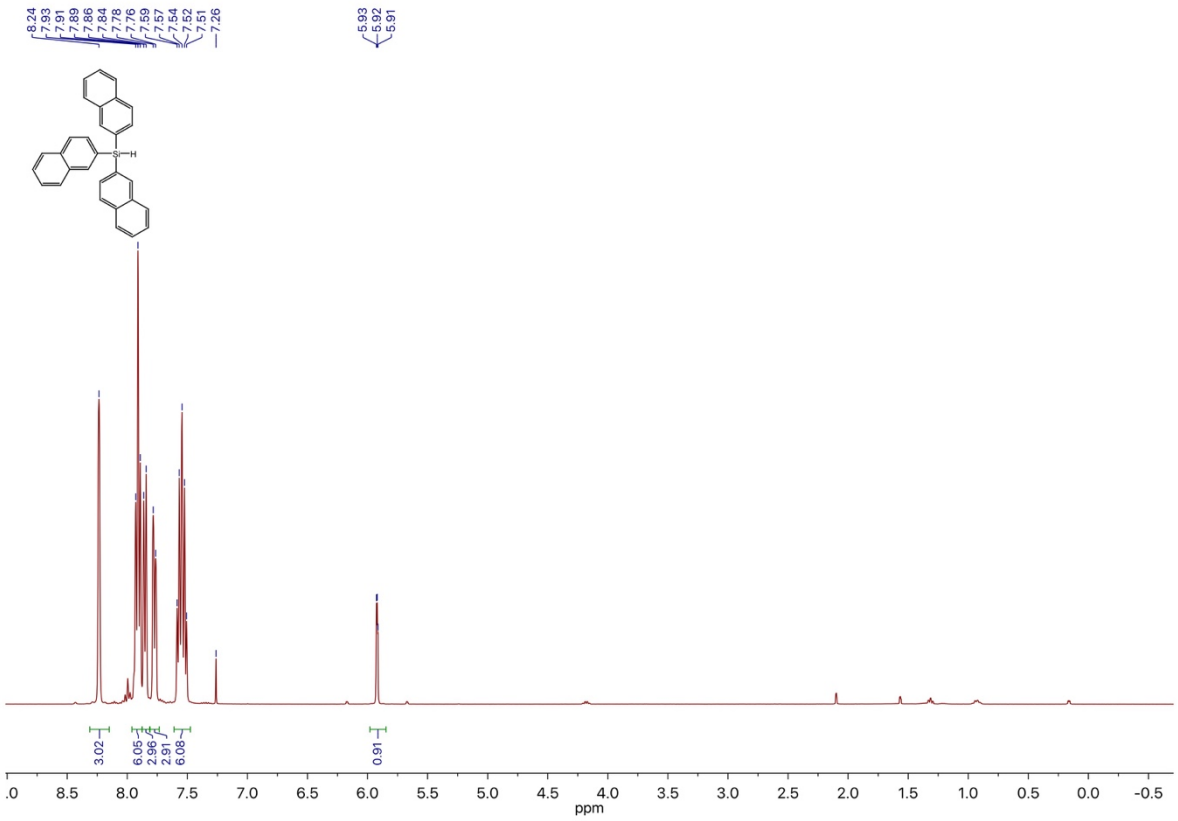


Figure S26: ^{1}H NMR spectrum of silane **7e** (400 MHz, $CDCl_3$).

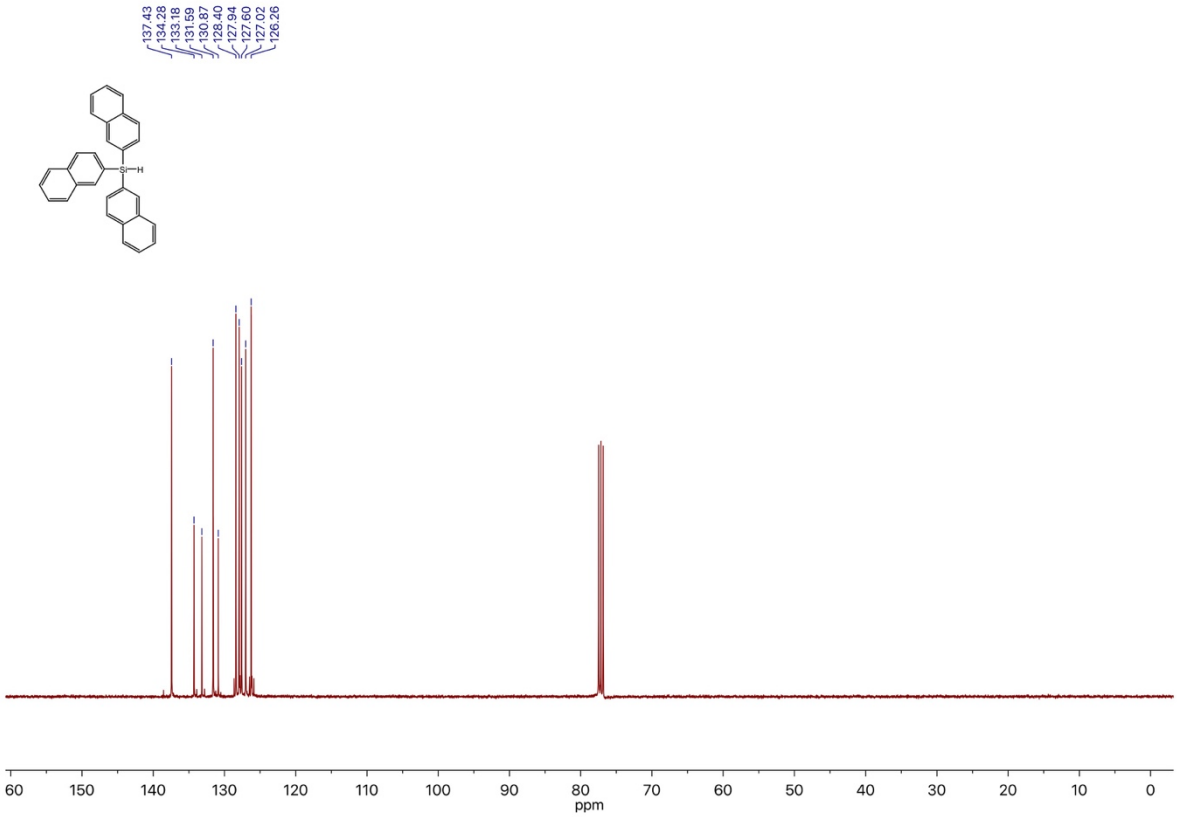


Figure S27: ^{13}C NMR spectrum of silane **7e** (101 MHz, $CDCl_3$).

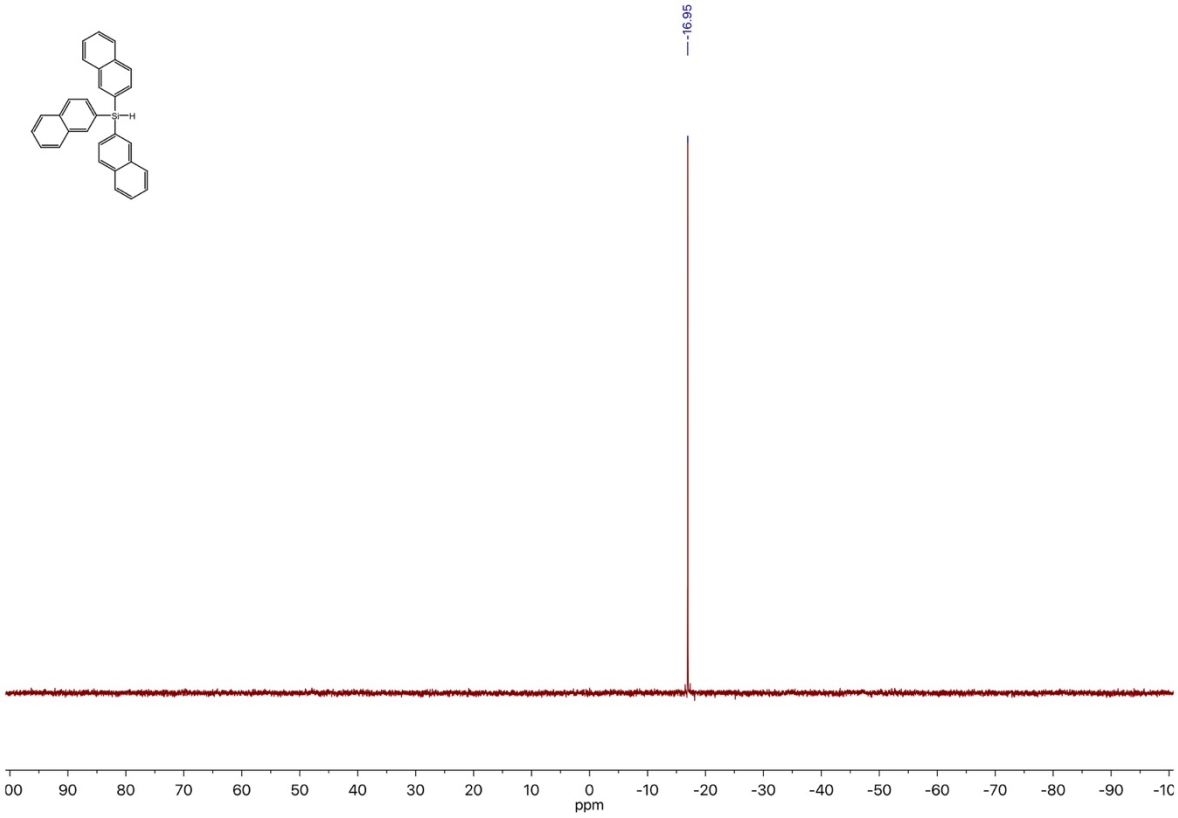


Figure S28: ^{29}Si NMR spectrum of silane **7e** (79 MHz, $CDCl_3$).

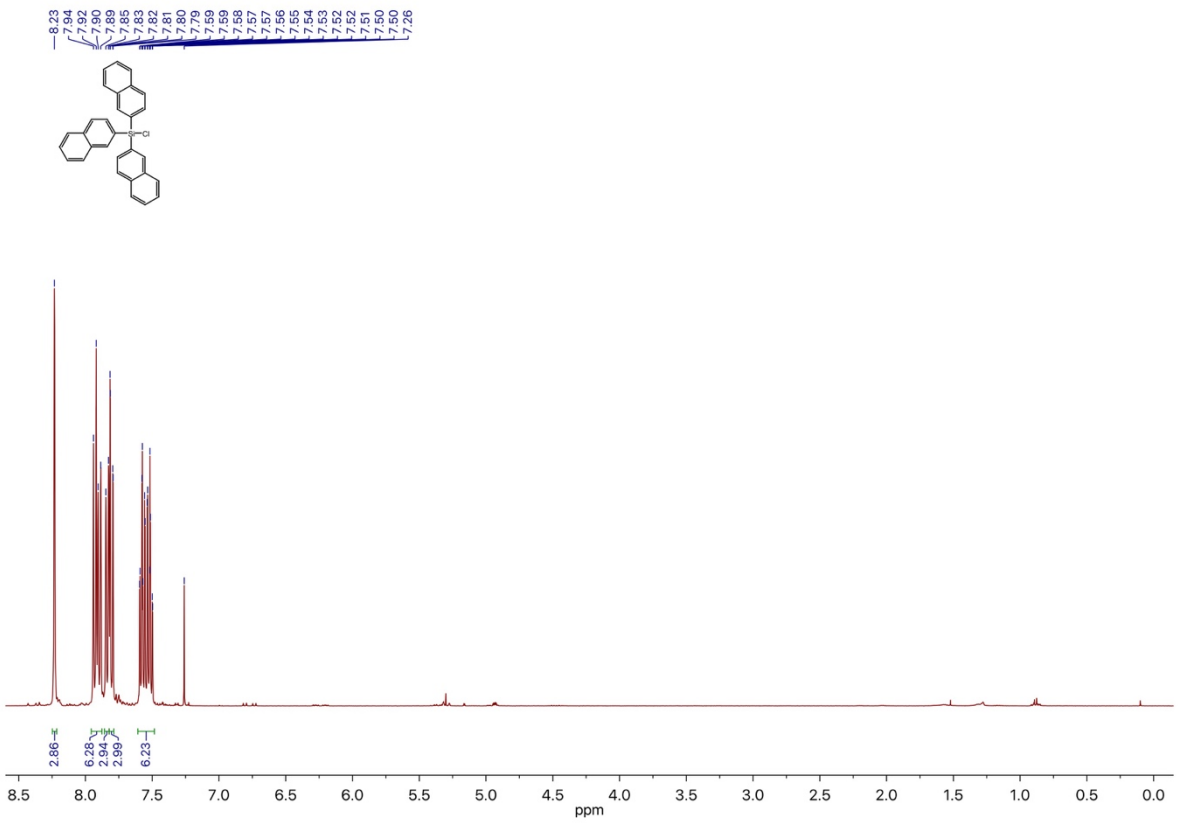


Figure S29: ^{1}H NMR spectrum of silyl chloride **2e** (400 MHz, $CDCl_3$).

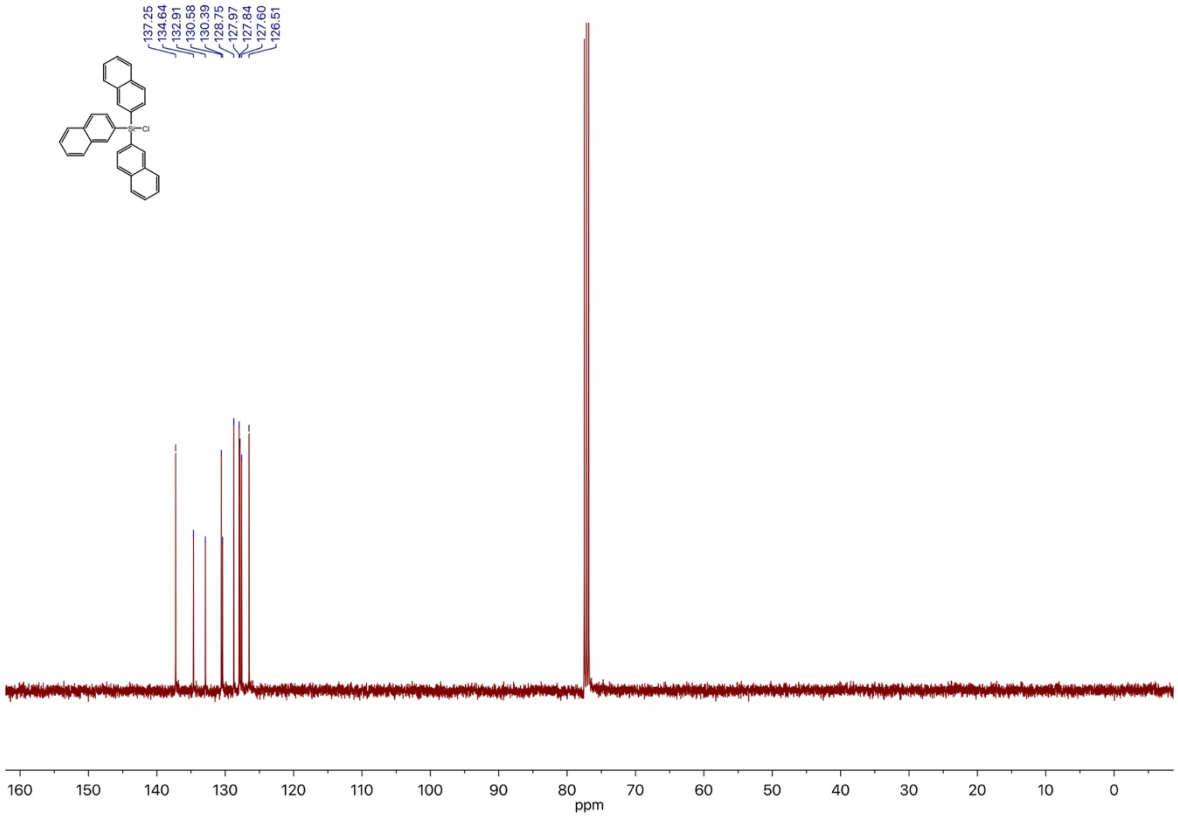


Figure S30: ^{13}C NMR spectrum of silyl chloride **2e** (101 MHz, $CDCl_3$).

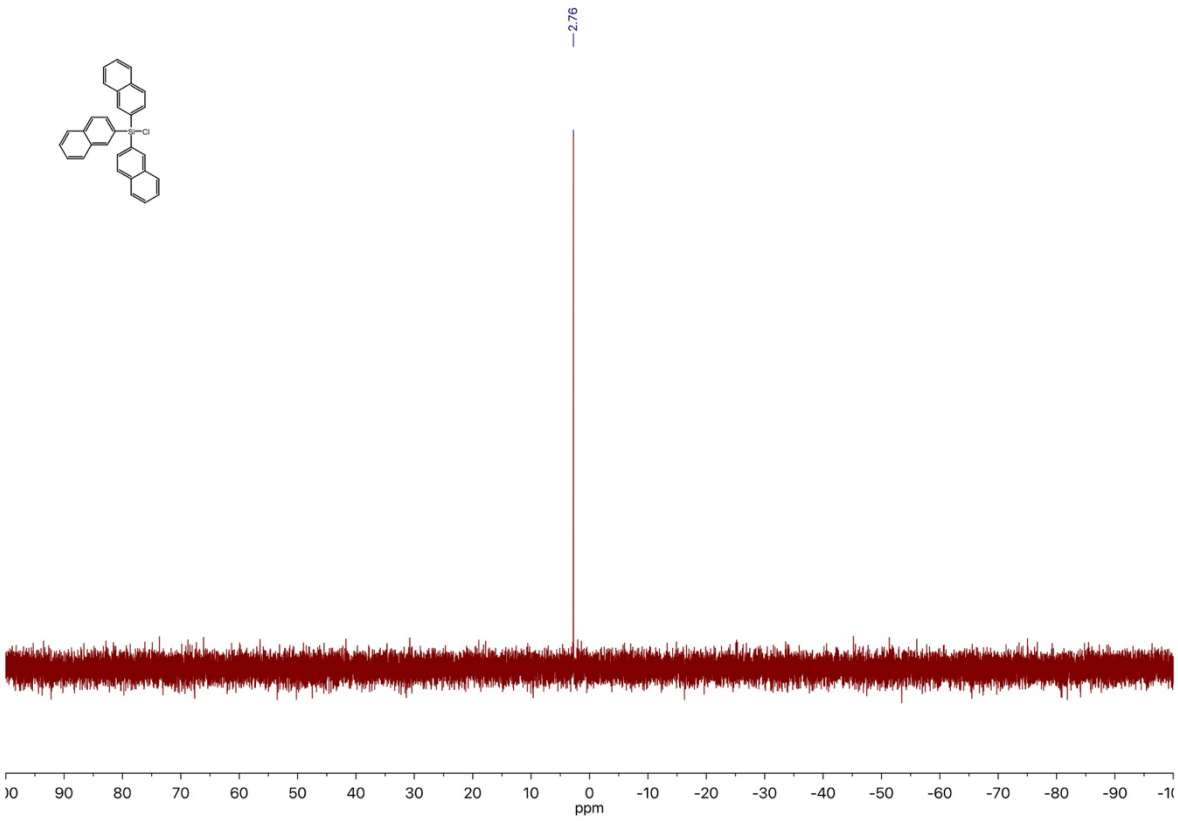


Figure S31: ^{29}Si NMR spectrum of silyl chloride **2e** (79 MHz, $CDCl_3$).

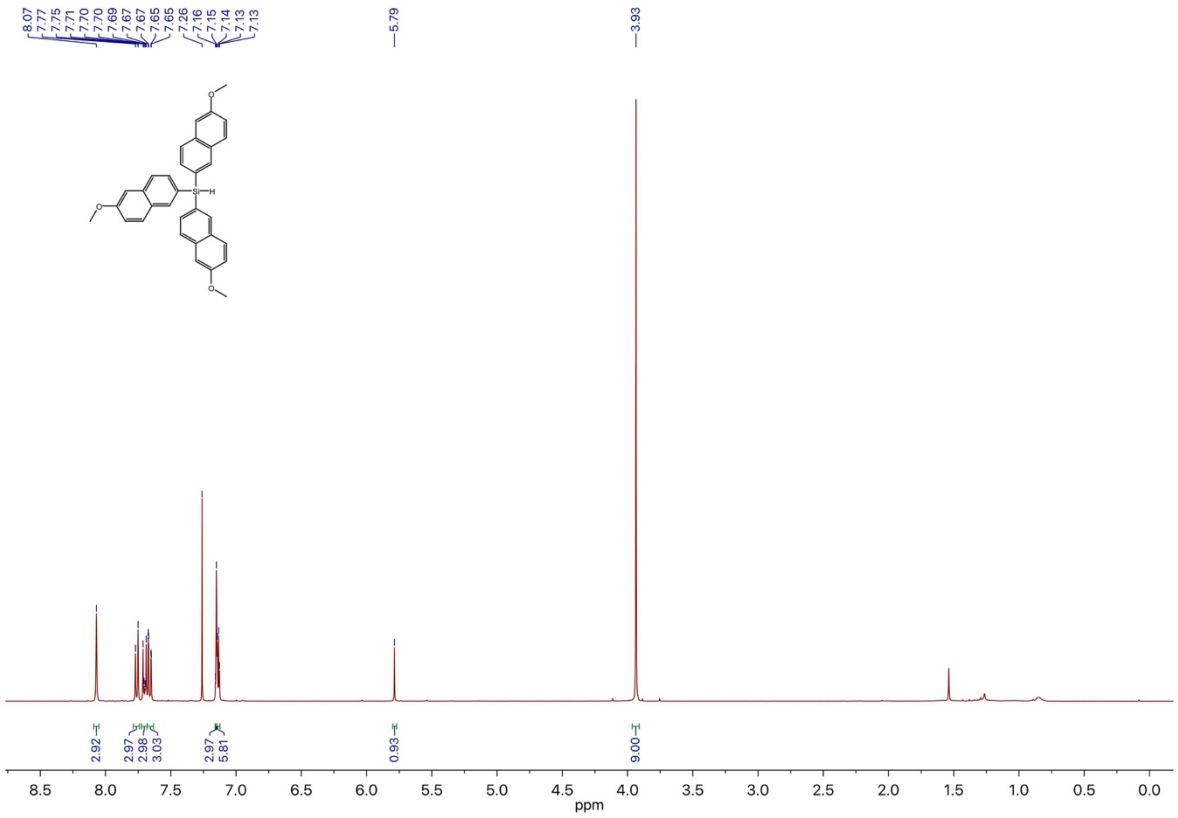


Figure S32: ^{1}H NMR spectrum of silane **7f** (400 MHz, $CDCl_3$).

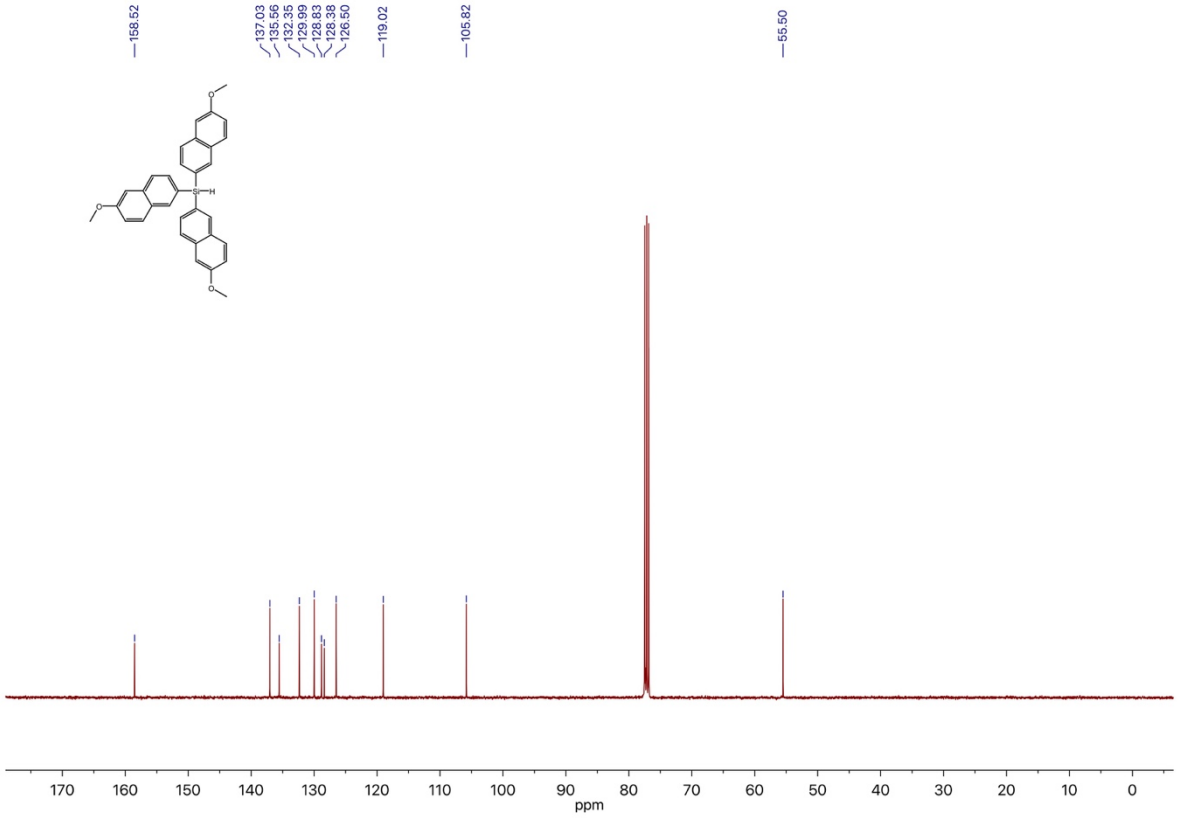


Figure S33: ^{13}C NMR spectrum of silane **7f** (101 MHz, $CDCl_3$).

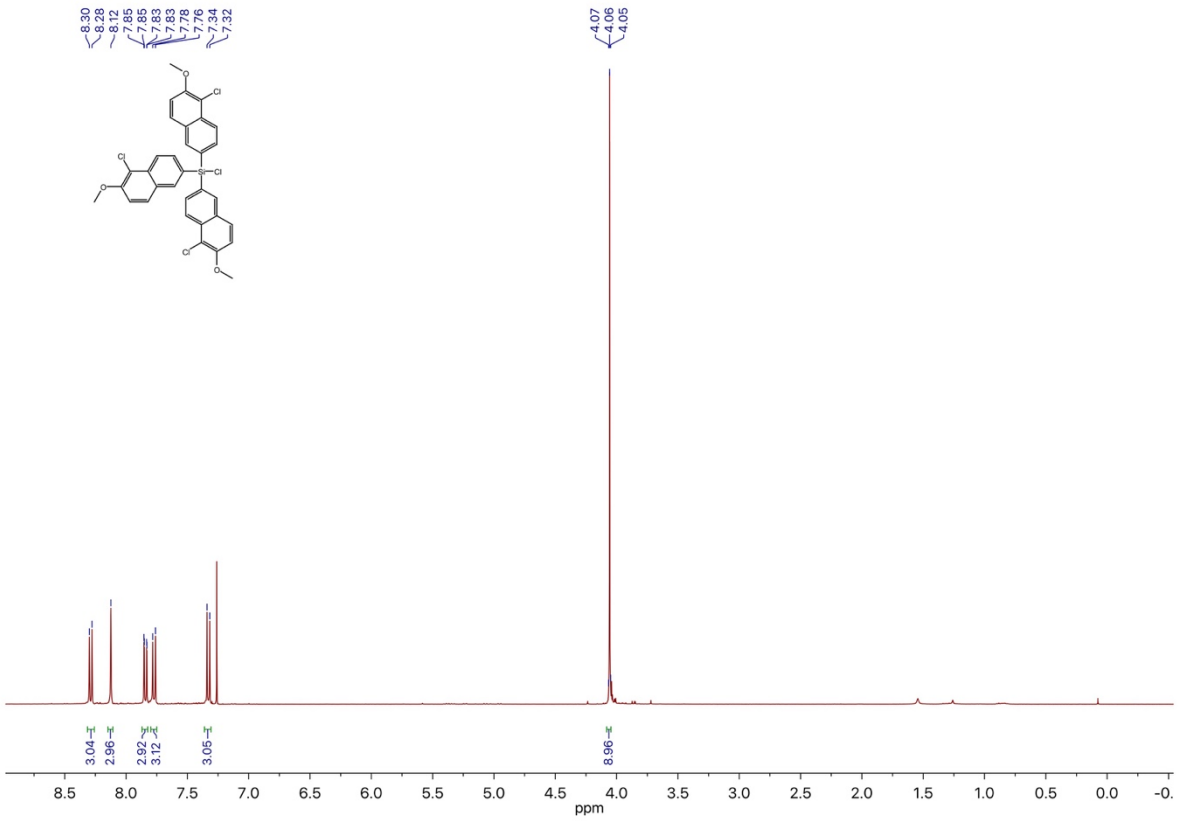


Figure S34: ^{1}H NMR spectrum of silyl chloride **2f** (400 MHz, $CDCl_3$).

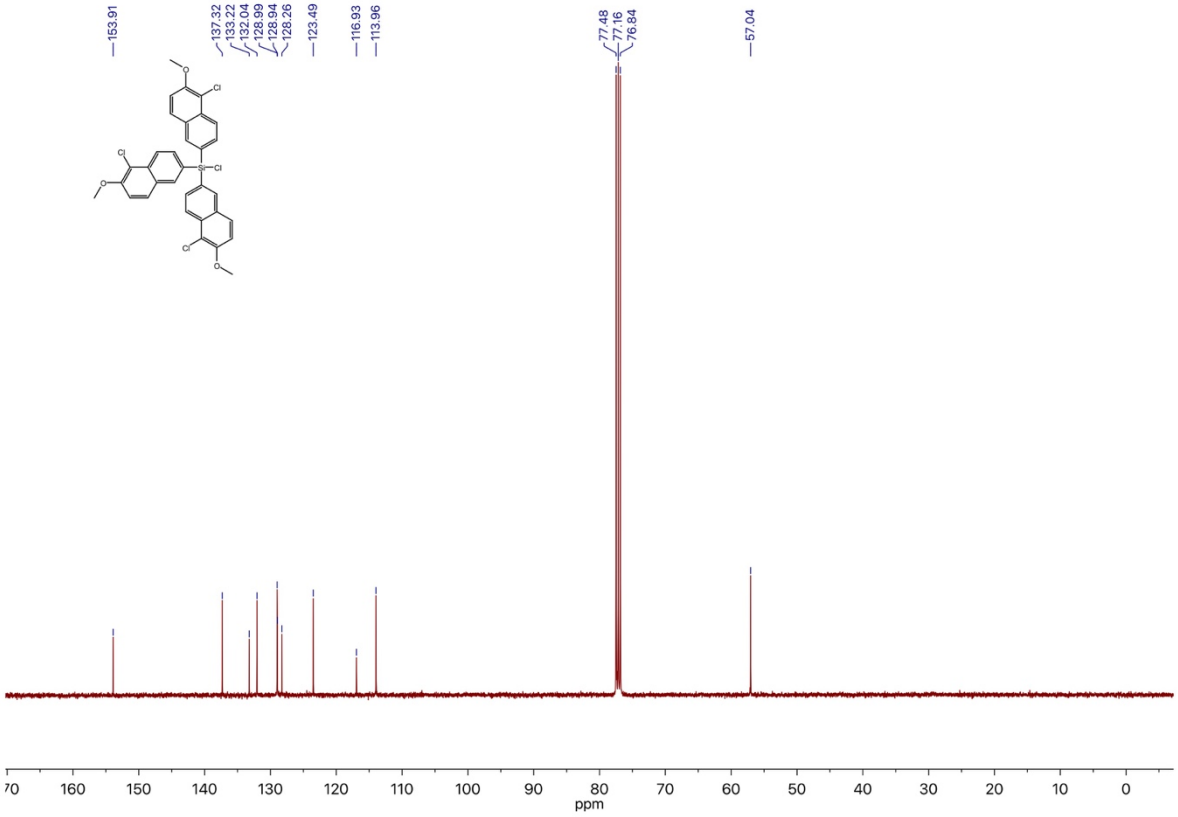


Figure S35: ^{13}C NMR spectrum of silyl chloride **2f** (101 MHz, $CDCl_3$).

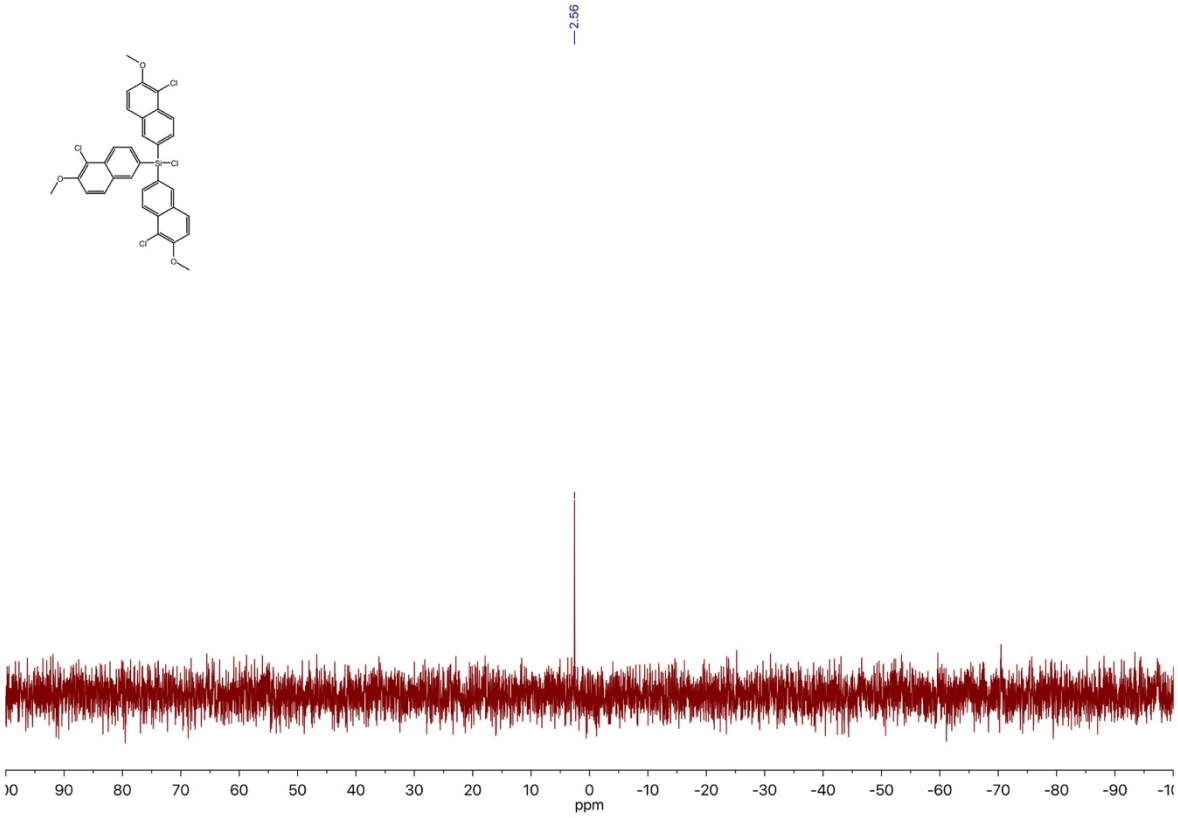


Figure S36: ^{29}Si NMR spectrum of silyl chloride **2f** (79 MHz, $CDCl_3$).

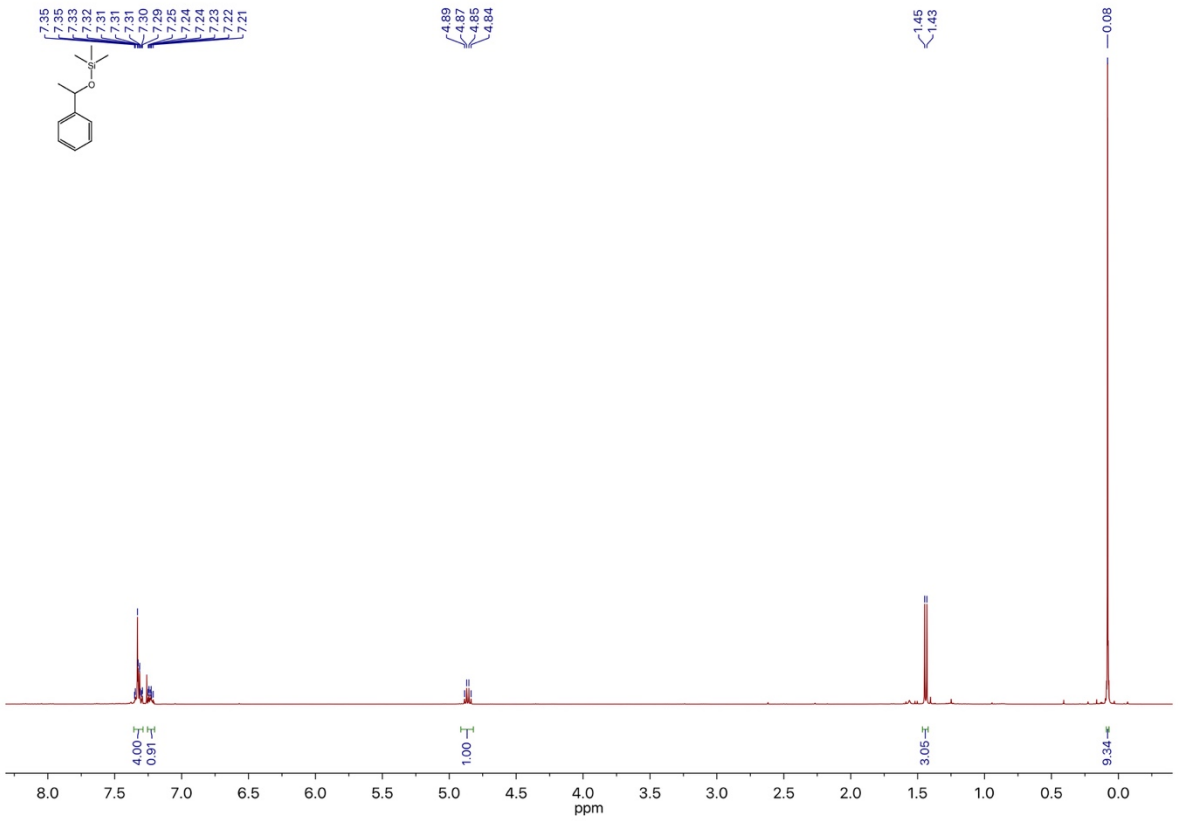


Figure S 37: ^{1}H NMR spectrum of silyl ether **5aa** (400 MHz, $CDCl_3$).

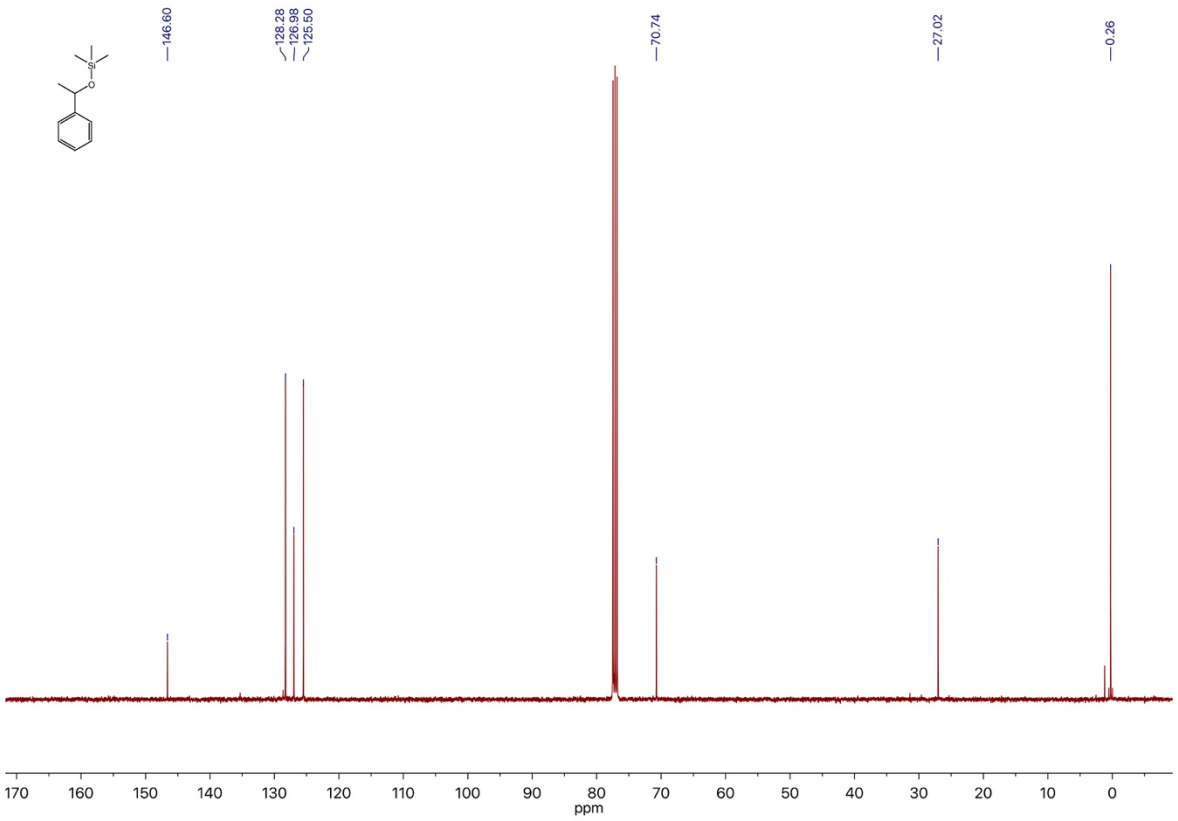


Figure S38: ^{13}C NMR spectrum of silyl ether **5ab** (101 MHz, $CDCl_3$).

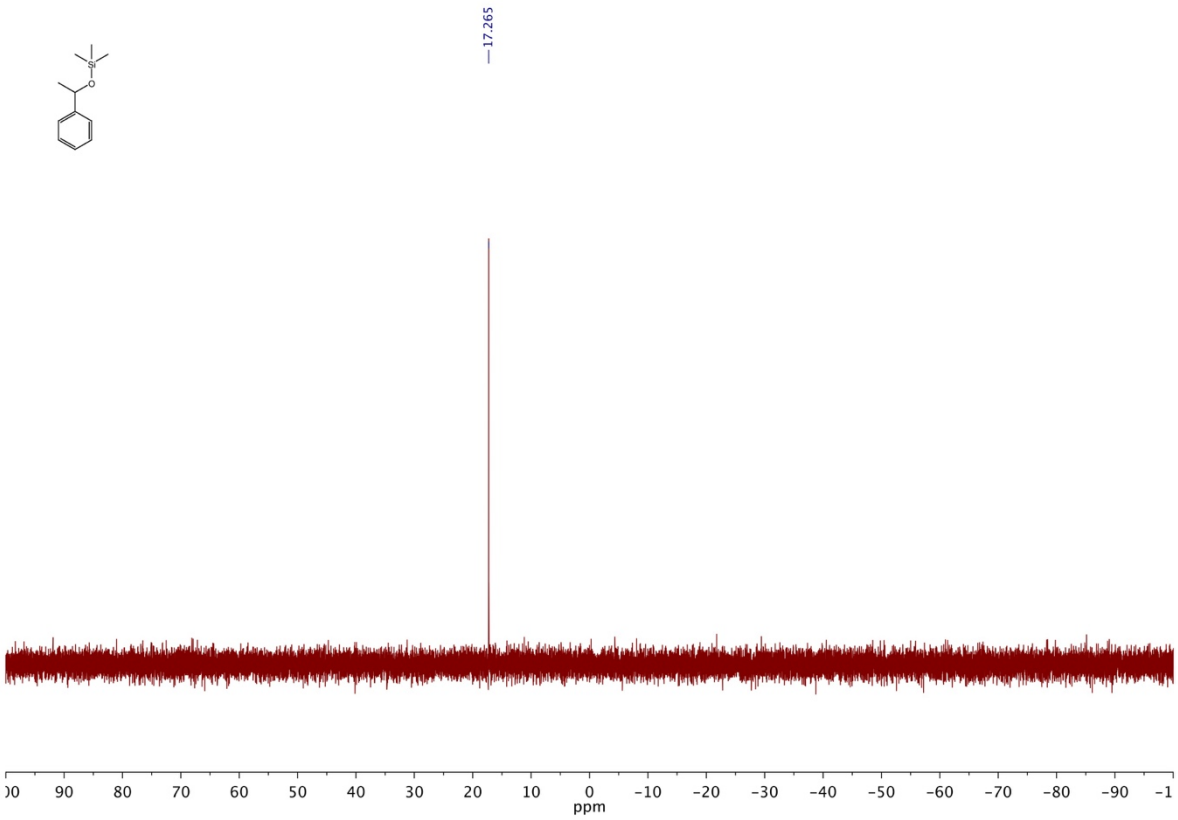


Figure S39: ^{29}Si NMR spectrum of silyl ether **5aa** (79 MHz, $CDCl_3$).

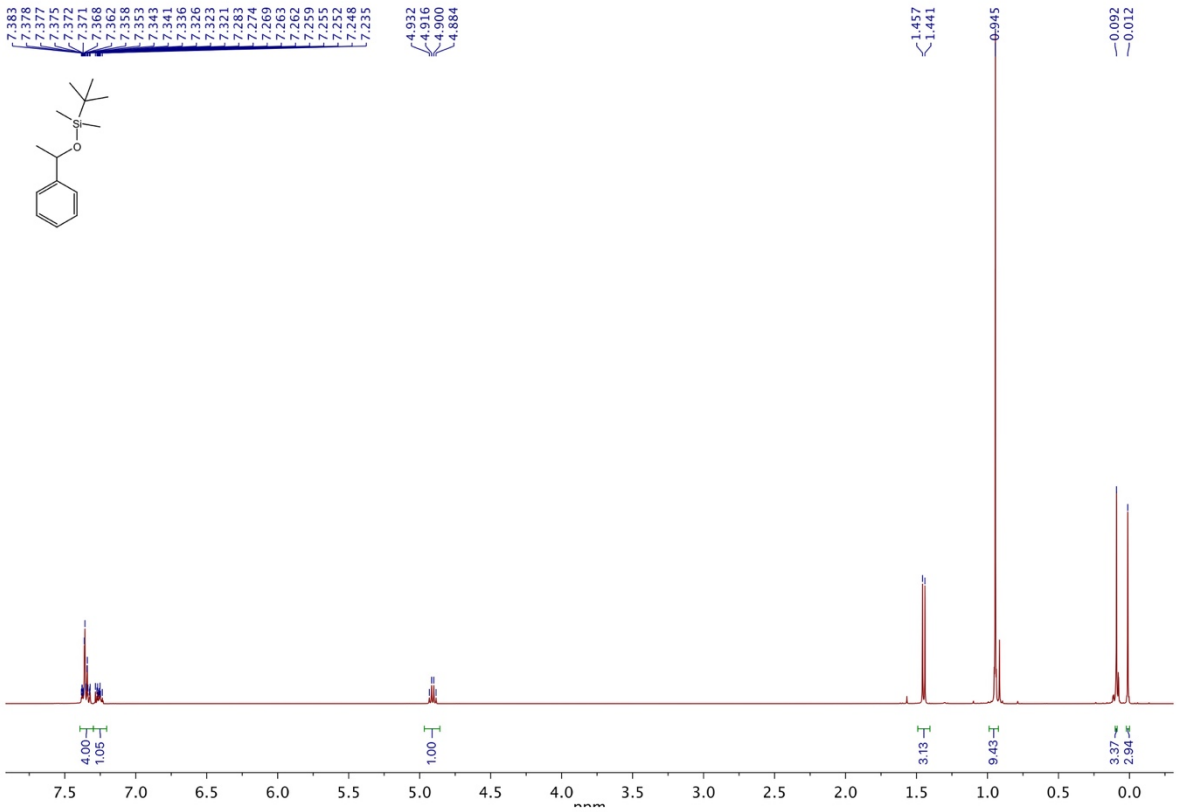


Figure S40: ^{1}H NMR spectrum of silyl ether **5ab** (400 MHz, $CDCl_3$).

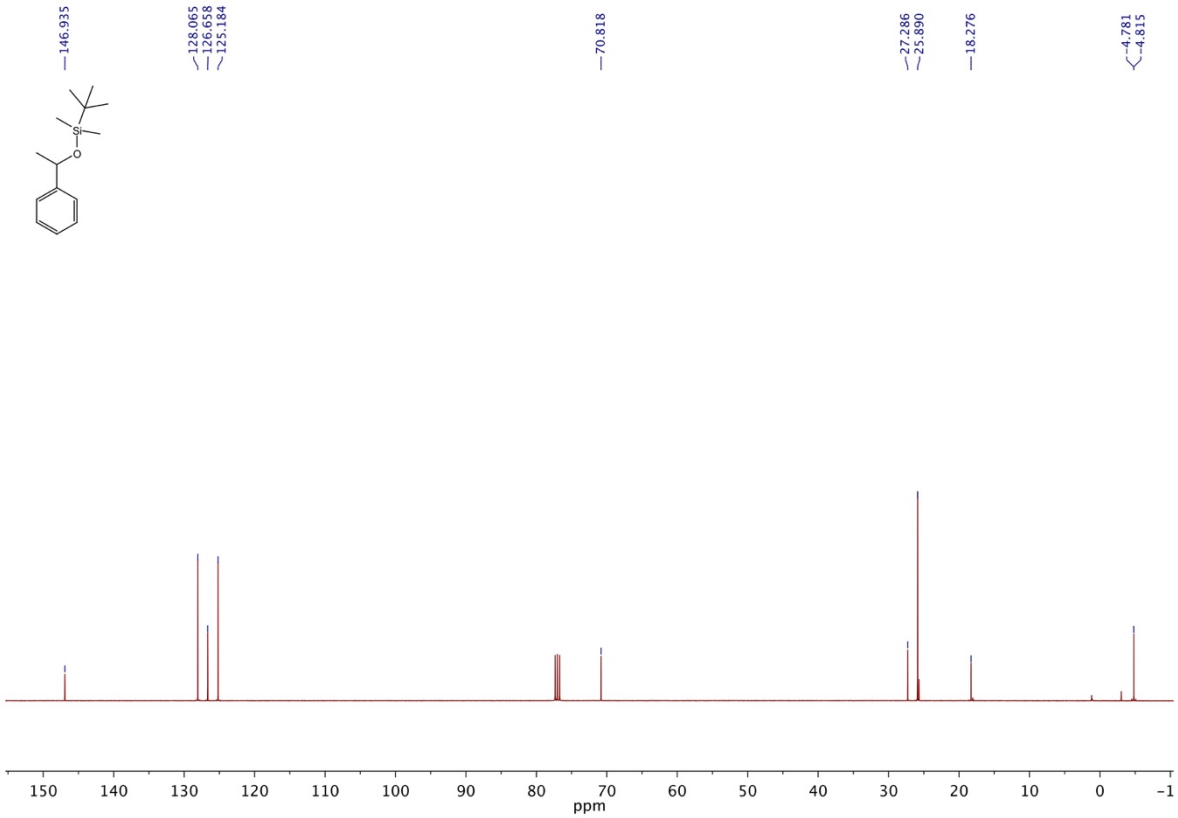


Figure S41: ^{13}C NMR spectrum of silyl ether **5ab** (101 MHz, $CDCl_3$).

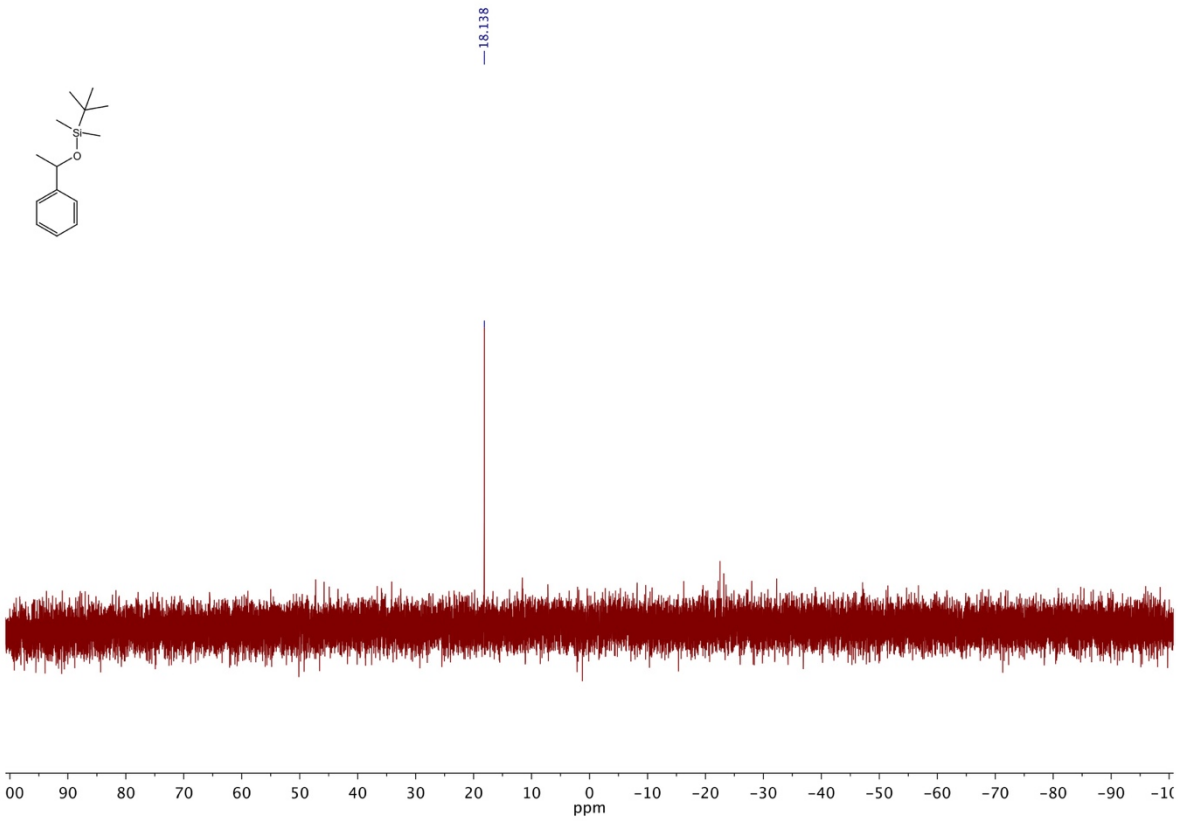


Figure S42: ^{29}Si NMR spectrum of silyl ether **5ab** (79 MHz, $CDCl_3$).

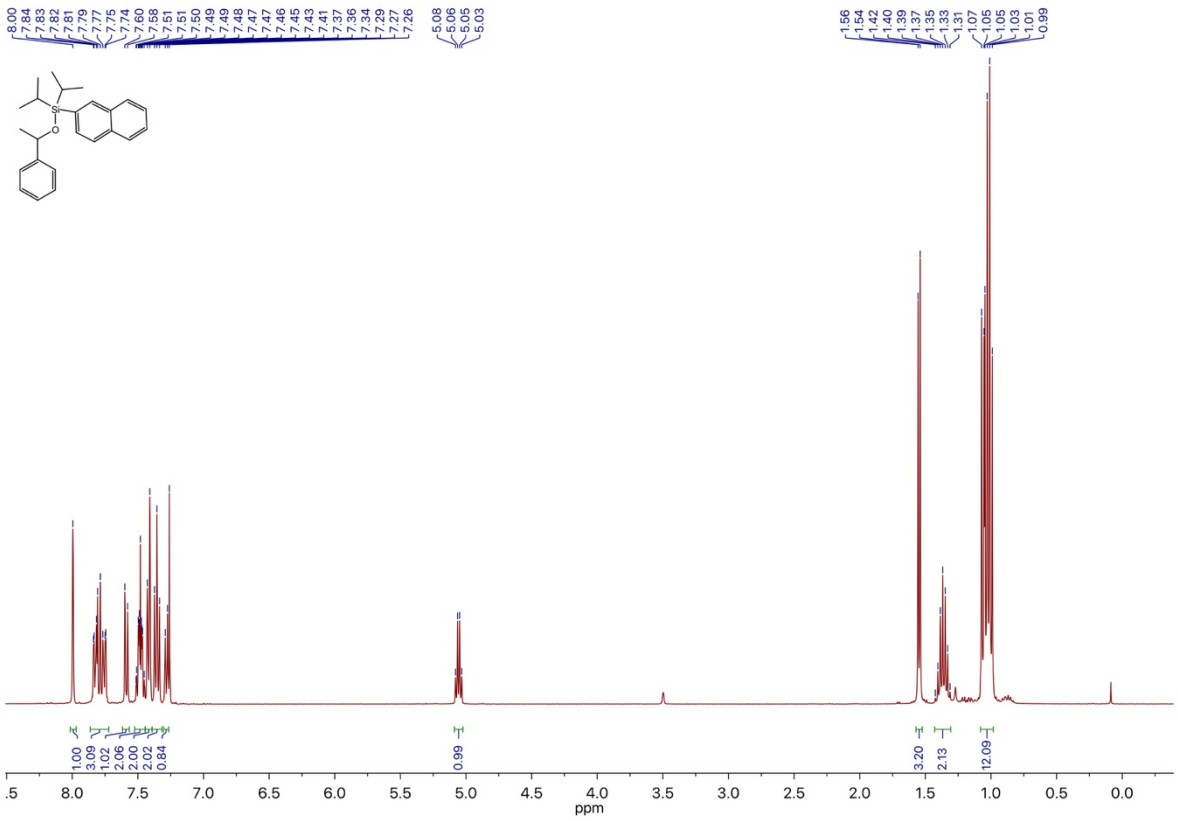


Figure S43: ^{1}H NMR spectrum of silyl ether **5ac** (400 MHz, $CDCl_3$).

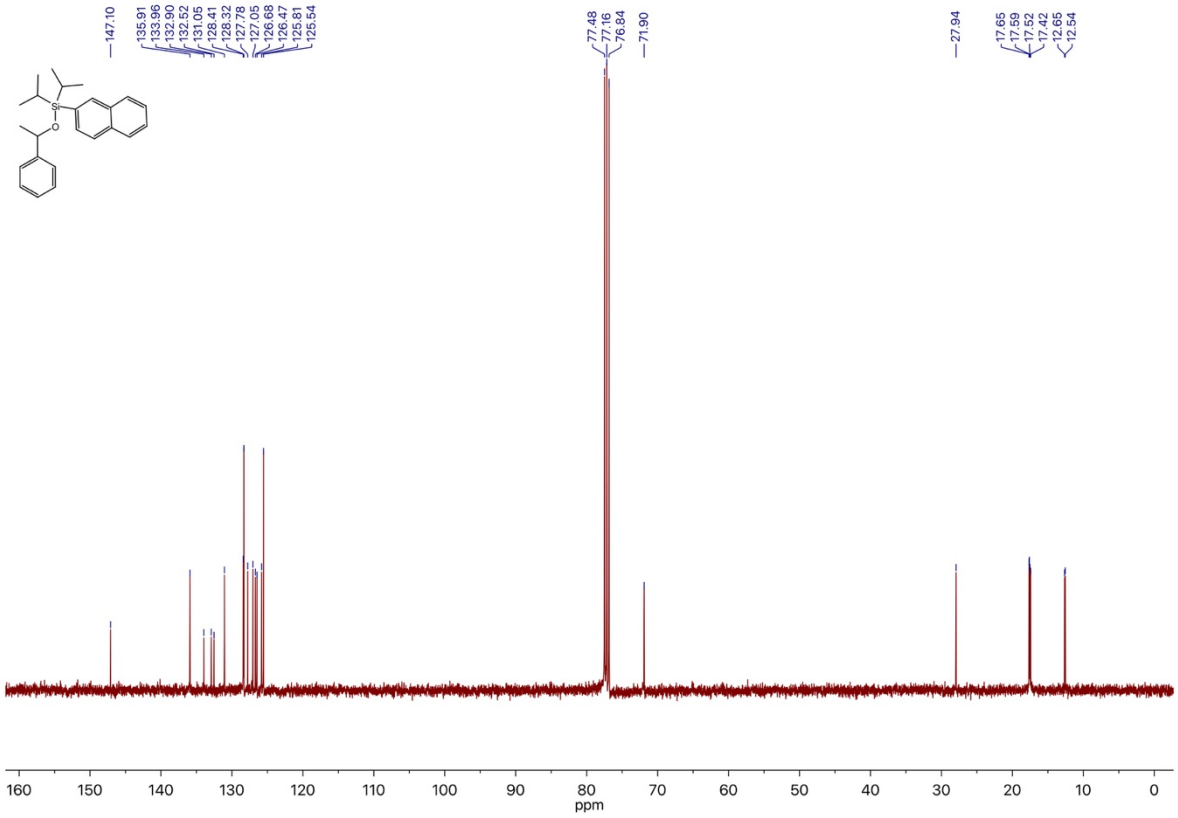


Figure S44: ^{13}C NMR spectrum of silyl ether **5ac** (101 MHz, $CDCl_3$).

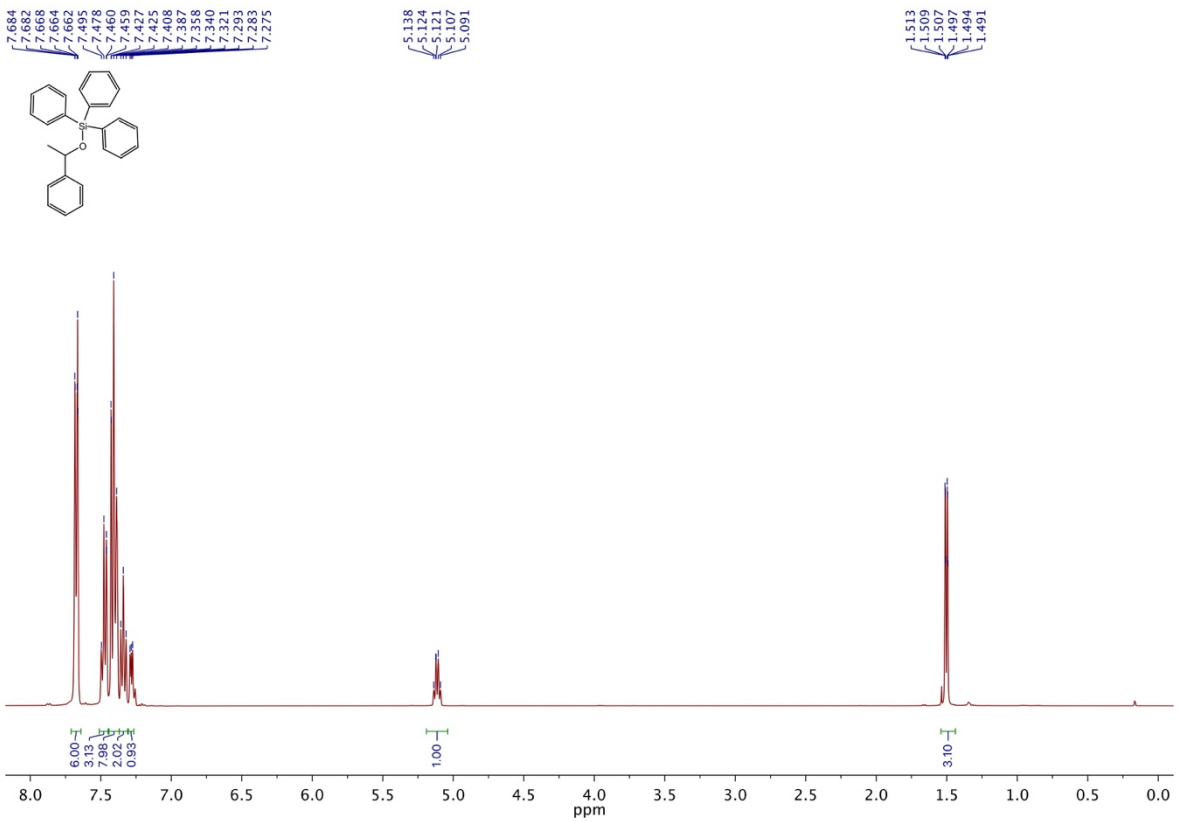


Figure S45: ^{1}H NMR spectrum of silyl ether **5ad** (400 MHz, $CDCl_3$).

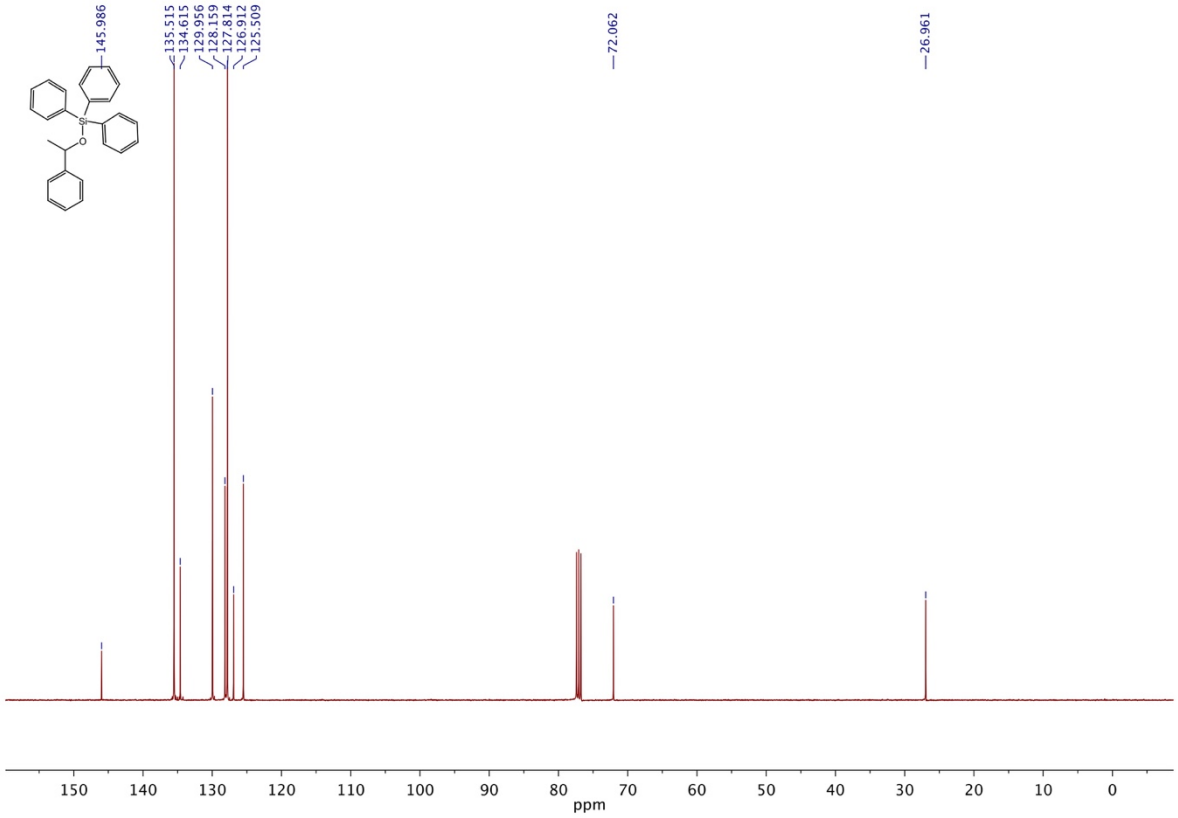


Figure S46: ^{13}C NMR spectrum of silyl ether **5ad** (101 MHz, $CDCl_3$).

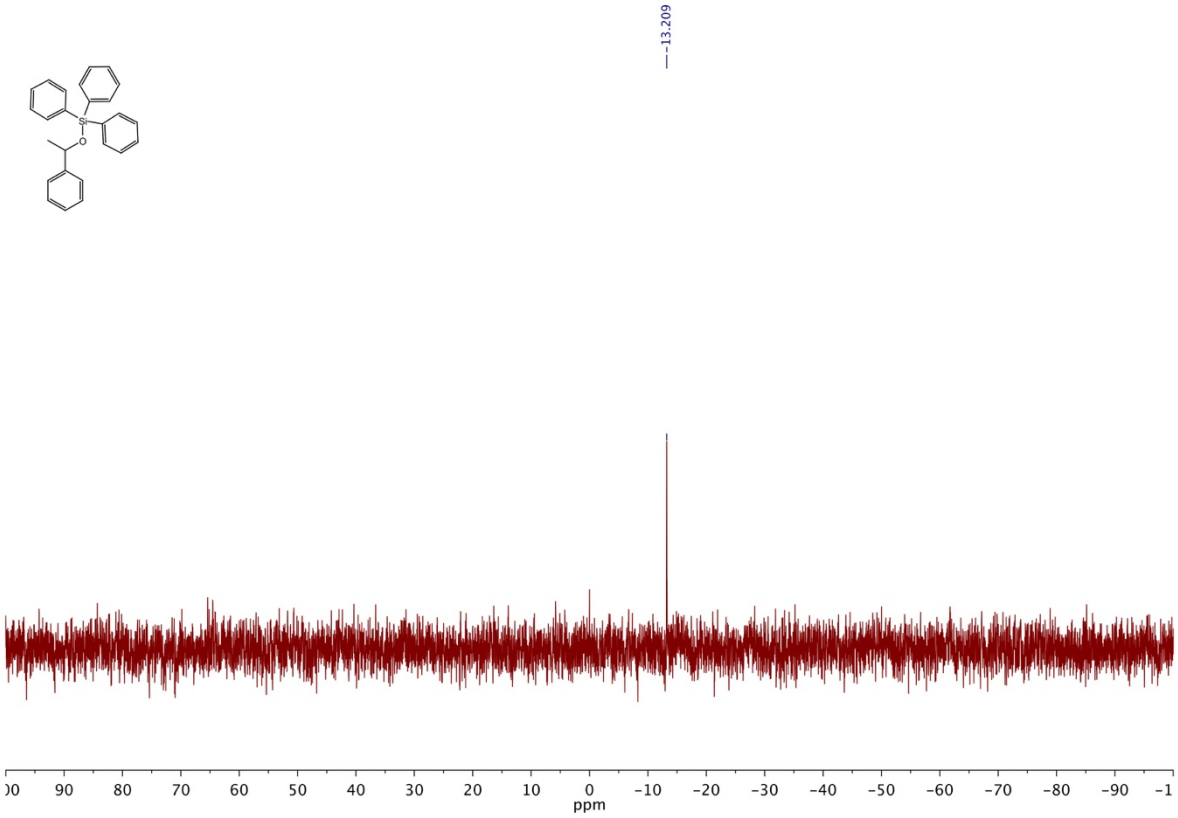


Figure S47: ^{29}Si NMR spectrum of silyl ether **5ad** (79 MHz, $CDCl_3$).

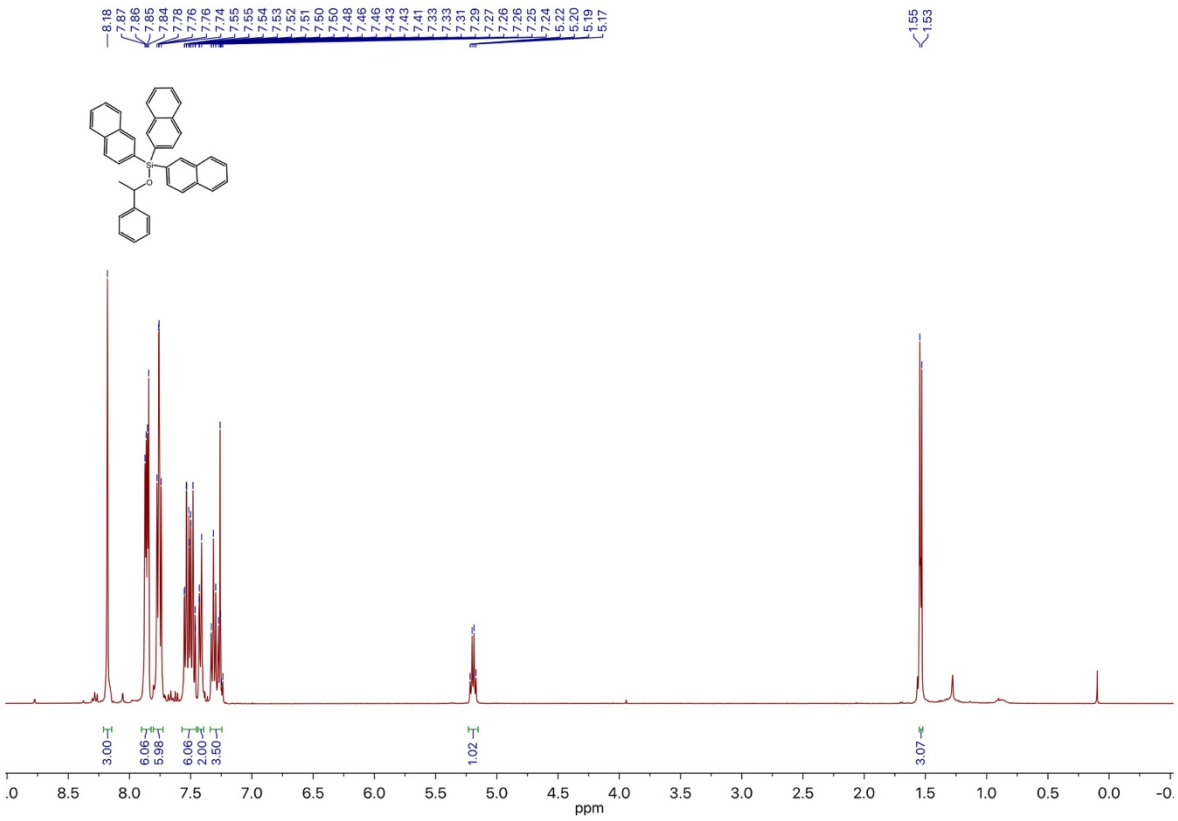


Figure S48: ^{1}H NMR spectrum of silyl ether **5ae** (400 MHz, $CDCl_3$).

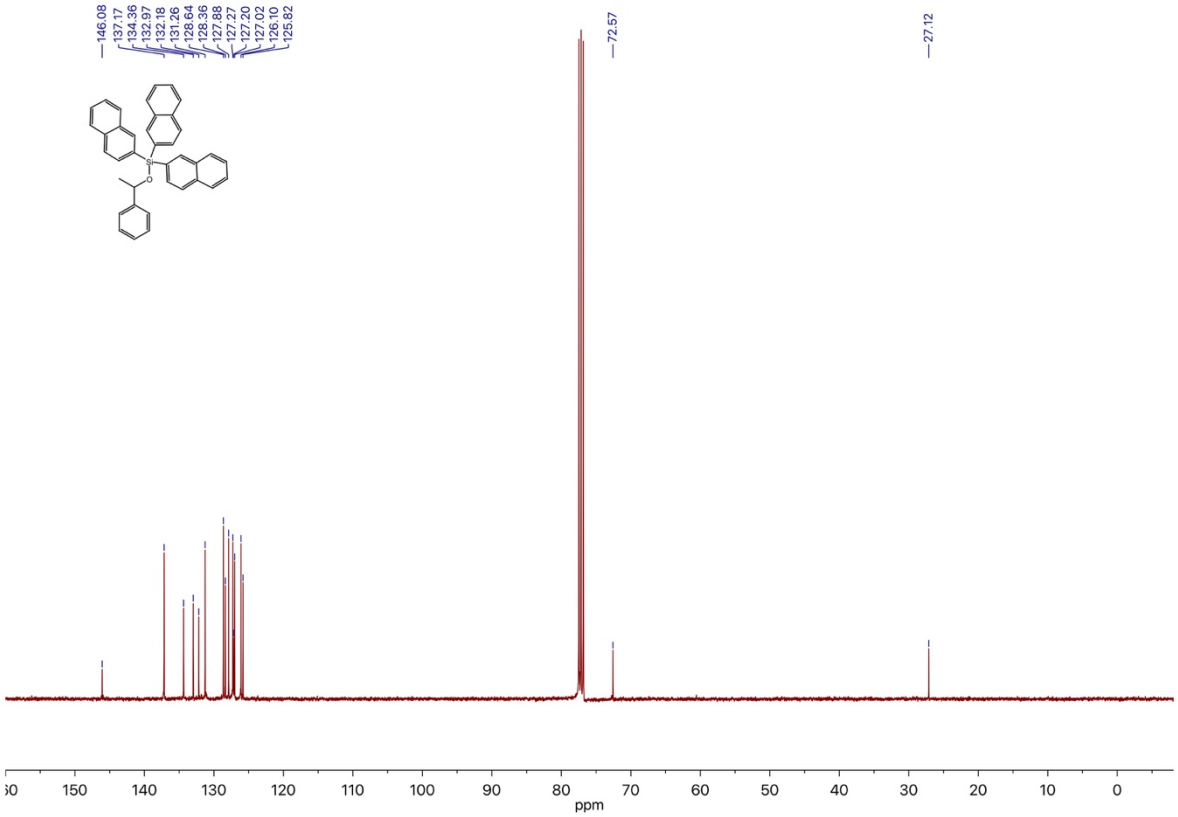


Figure S49: ^{13}C NMR spectrum of silyl ether **5ae** (101 MHz, $CDCl_3$).

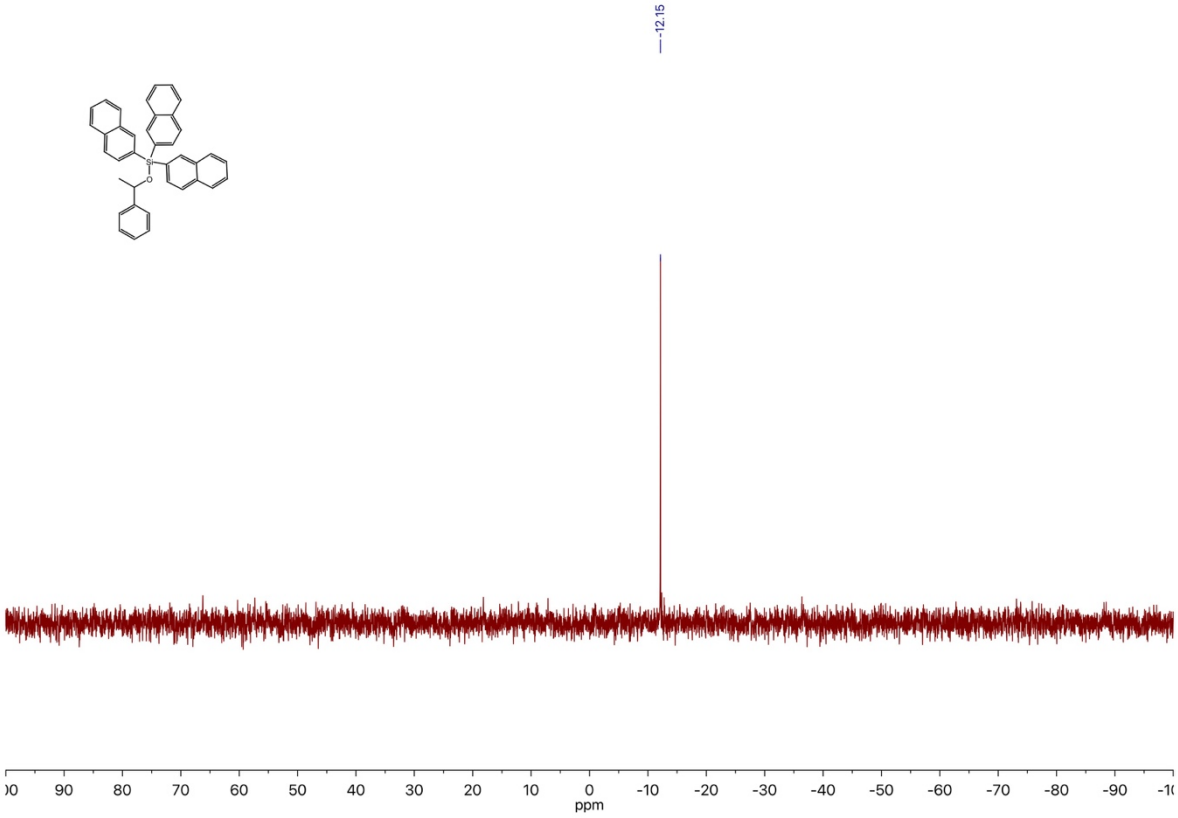


Figure S50: ^{29}Si NMR spectrum of silyl ether **5ae** (79 MHz, $CDCl_3$).

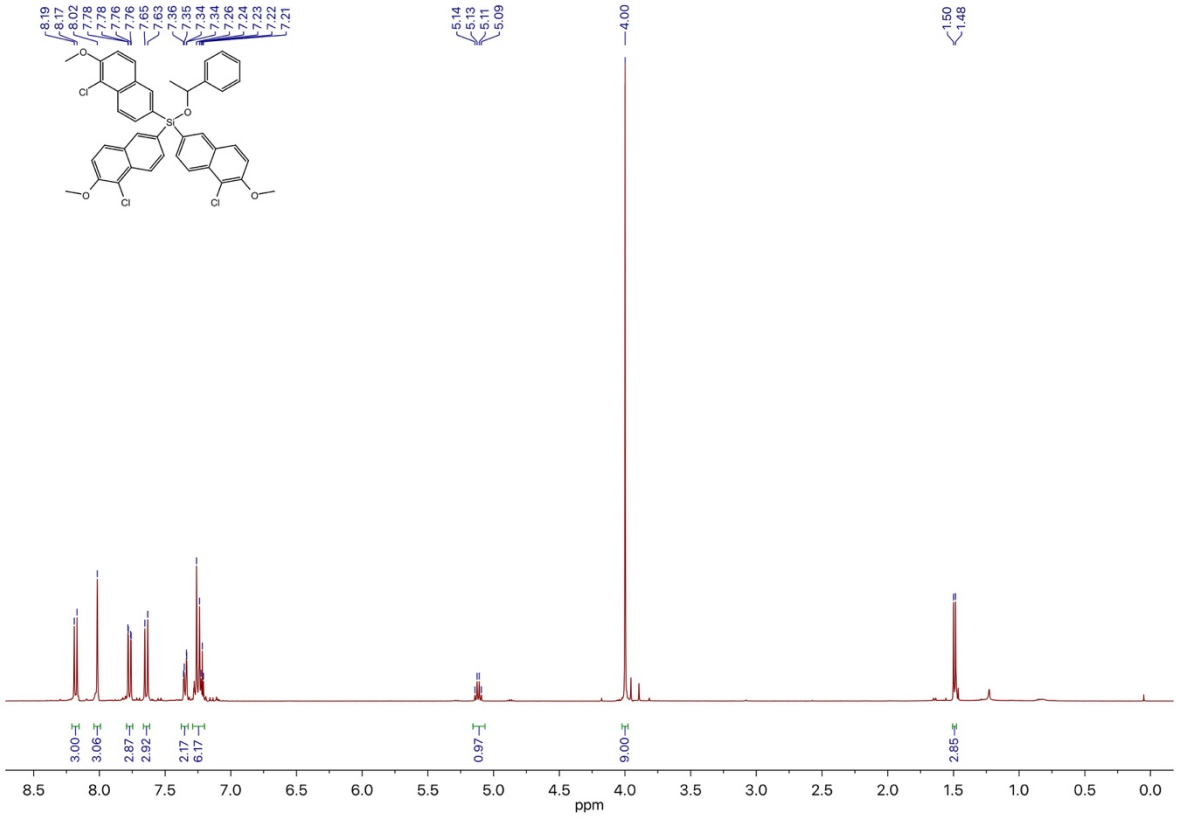


Figure S51: ^{1}H NMR spectrum of silyl ether **5af** (400 MHz, $CDCl_3$).

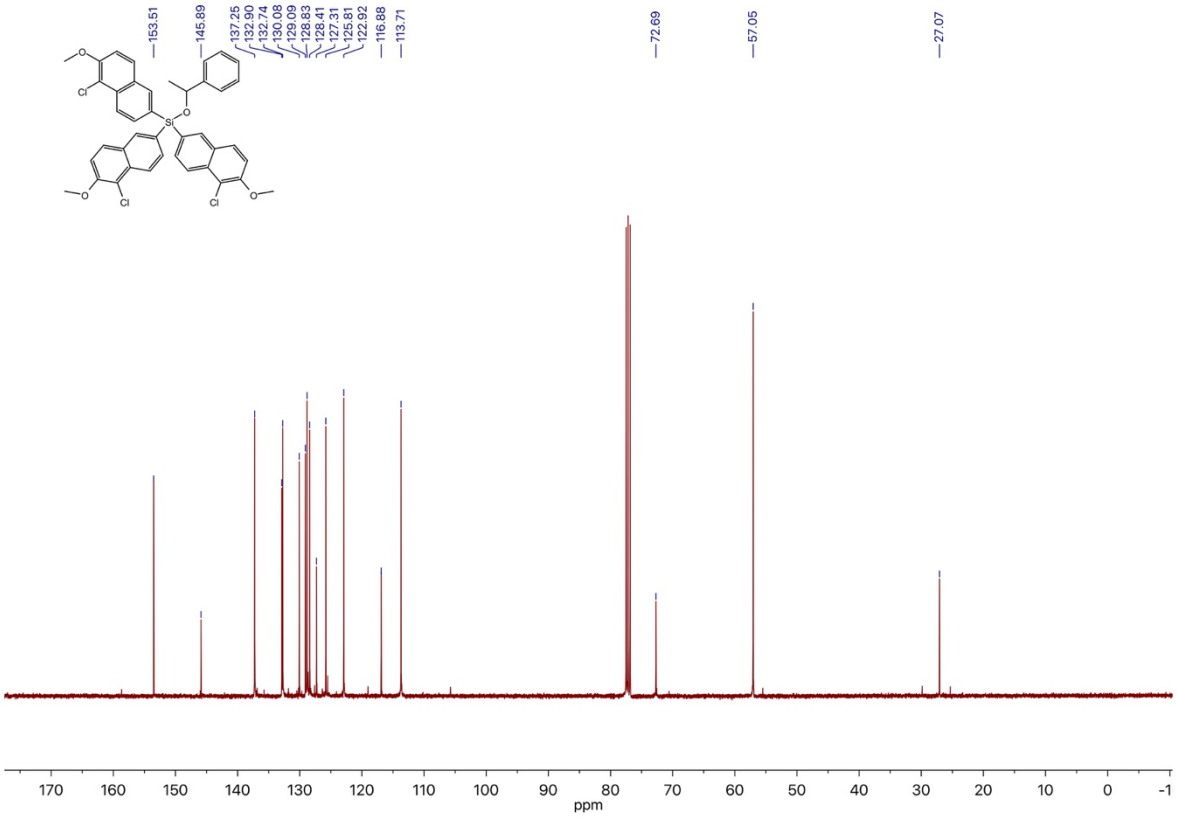


Figure S52: ^{13}C NMR spectrum of silyl ether **5af** (101 MHz, $CDCl_3$).

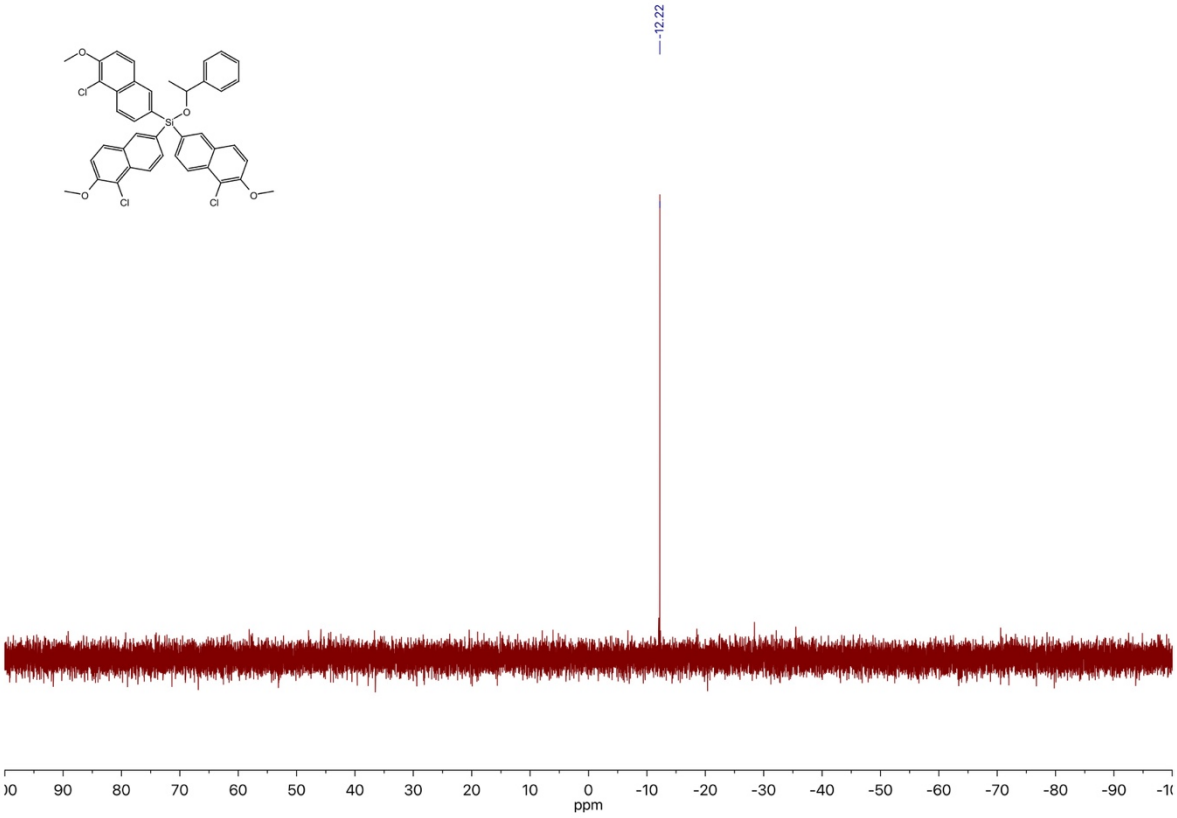


Figure S53: ^{29}Si NMR spectrum of silyl ether **5af** (79 MHz, $CDCl_3$).

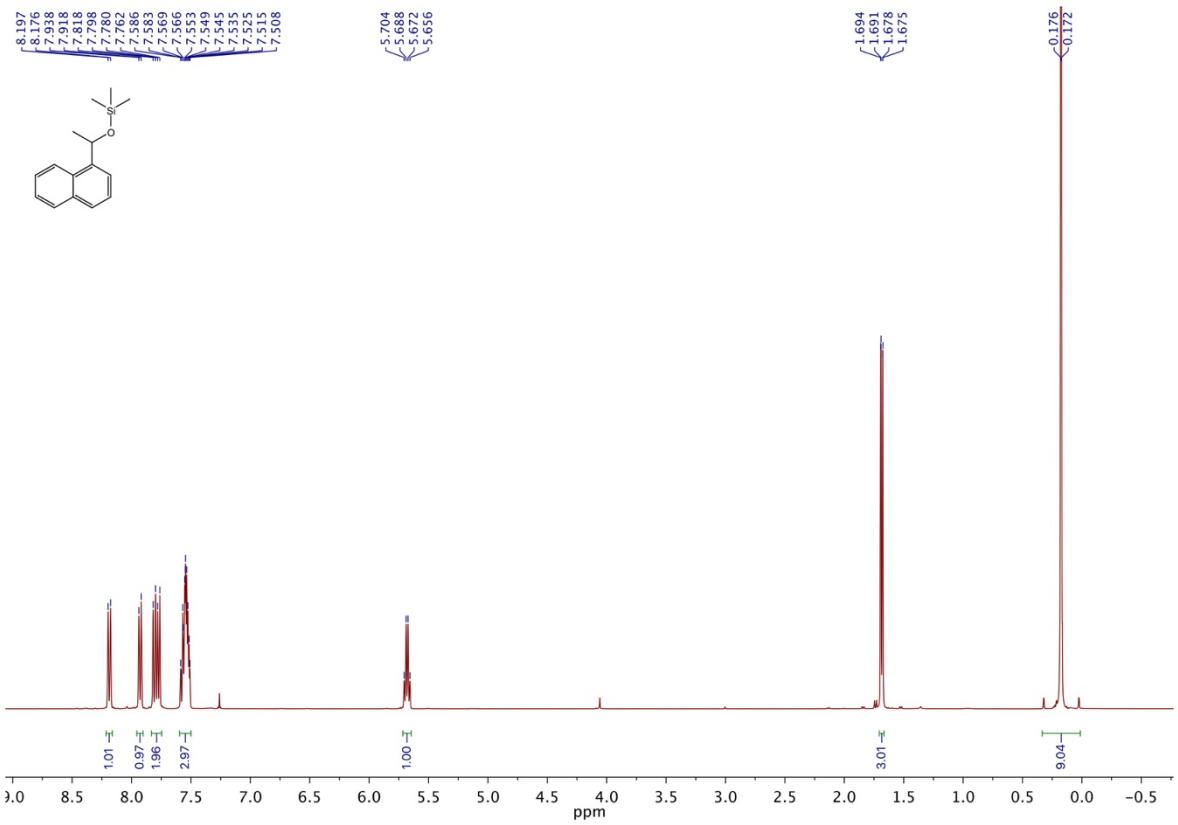


Figure S54: ^{1}H NMR spectrum of silyl ether **5ba** (400 MHz, $CDCl_3$).

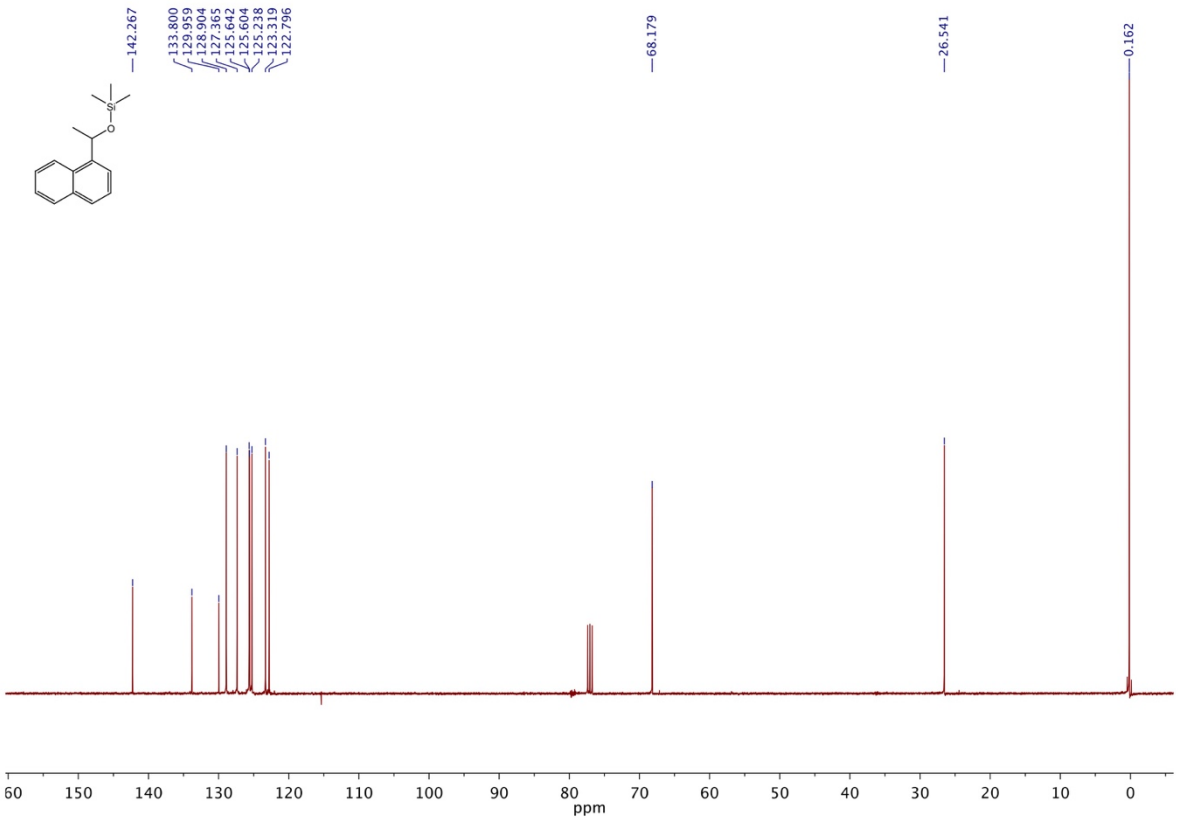


Figure S55: ^{13}C NMR spectrum of silyl ether **5ba** (101 MHz, $CDCl_3$).

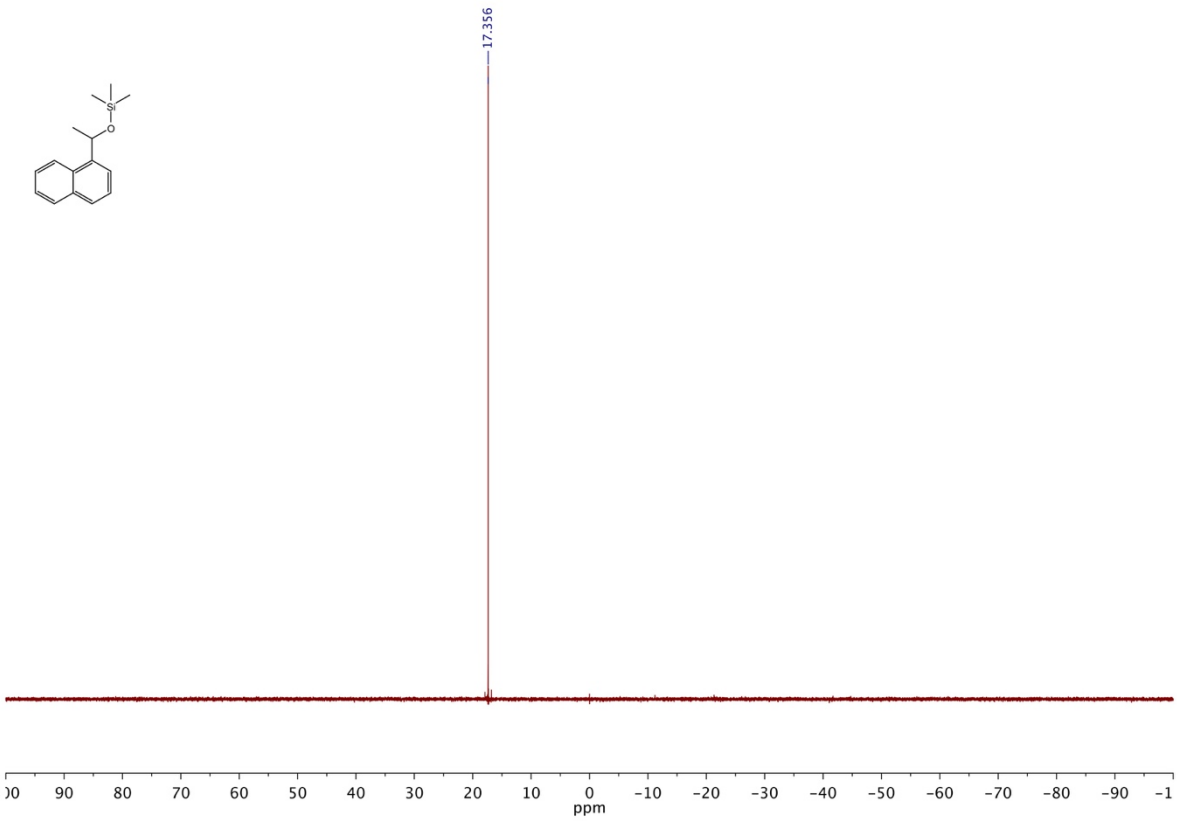


Figure S56: ^{29}Si NMR spectrum of silyl ether **5ba** (79 MHz, $CDCl_3$).

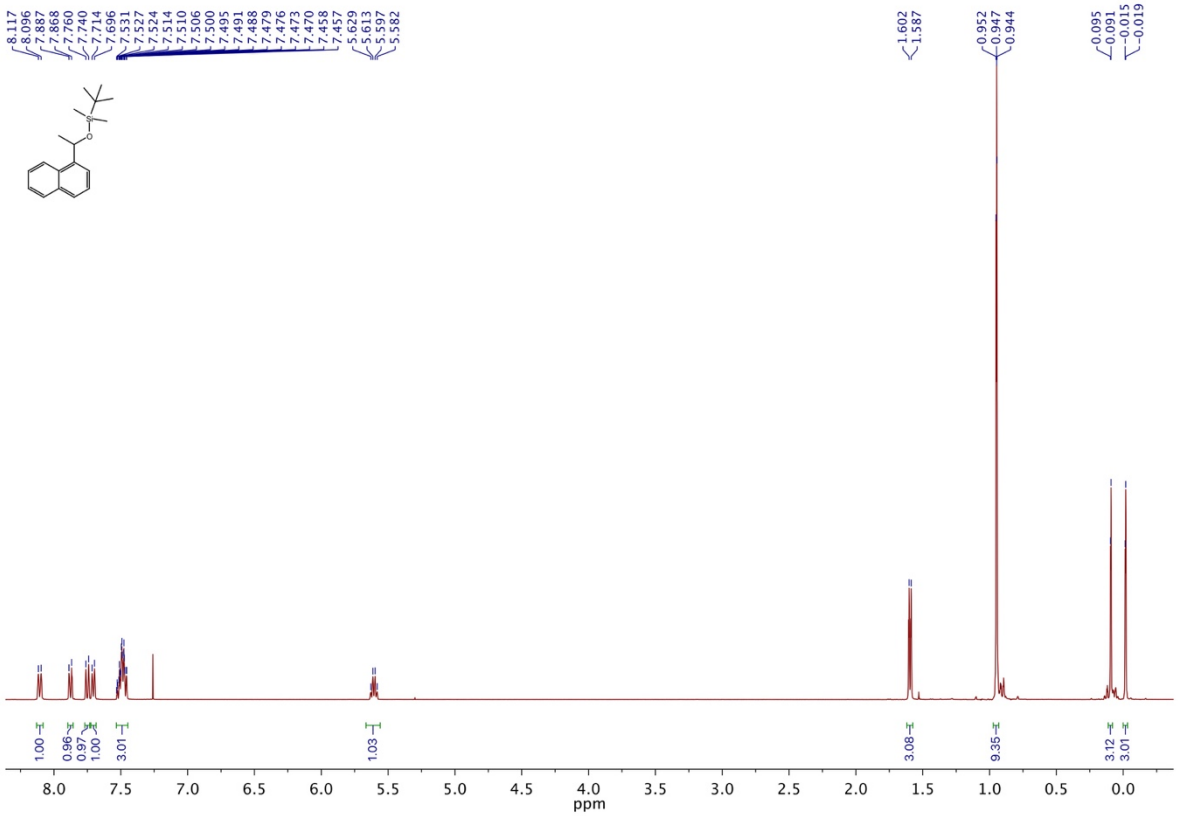


Figure S57: ^{1}H NMR spectrum of silyl ether **5bb** (400 MHz, $CDCl_3$).

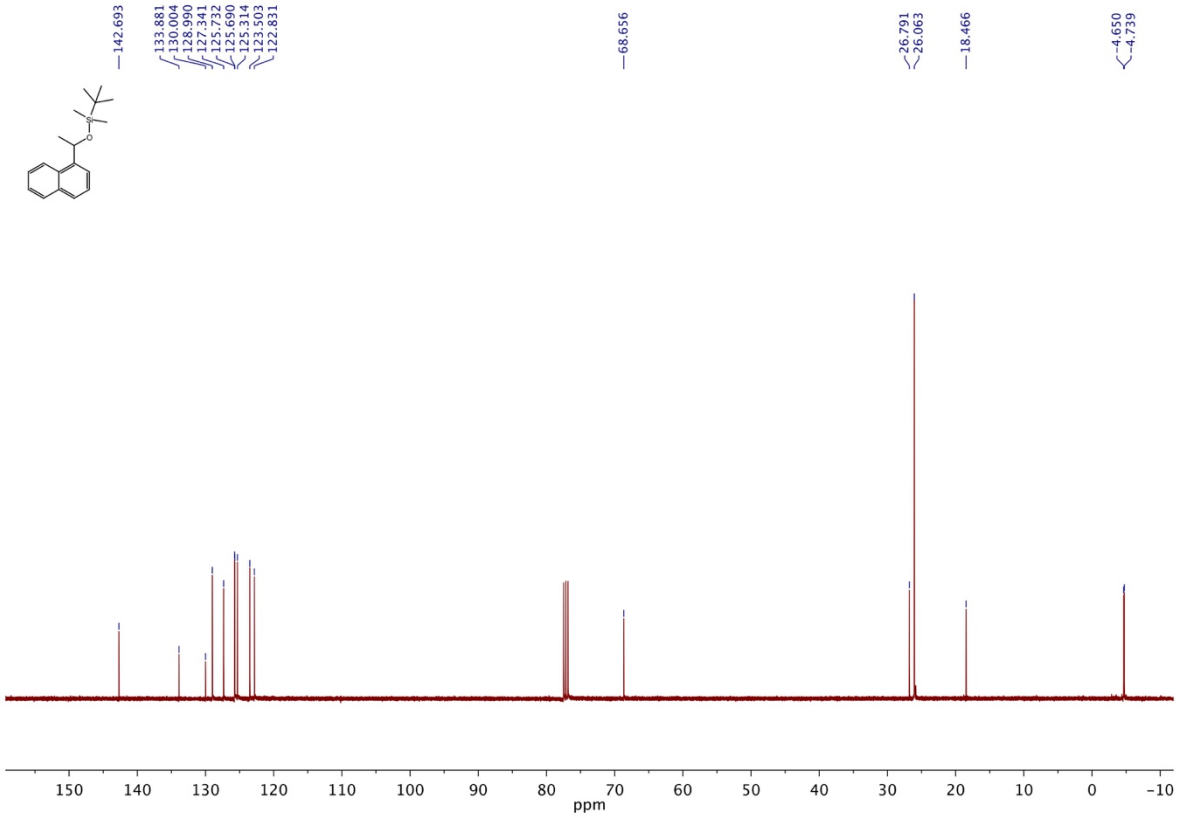


Figure S58: ^{13}C NMR spectrum of silyl ether **5bb** (101 MHz, $CDCl_3$).

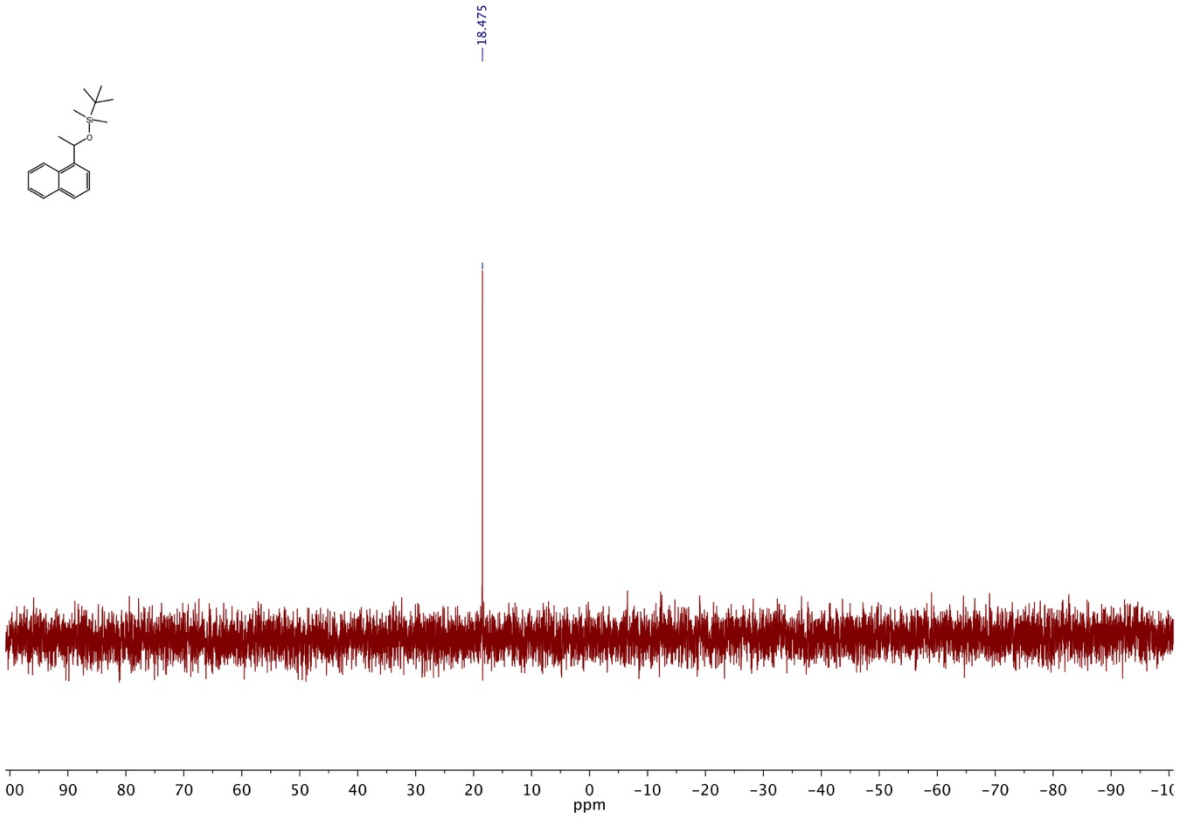


Figure S59: ^{29}Si NMR spectrum of silyl ether **5bb** (79 MHz, $CDCl_3$).

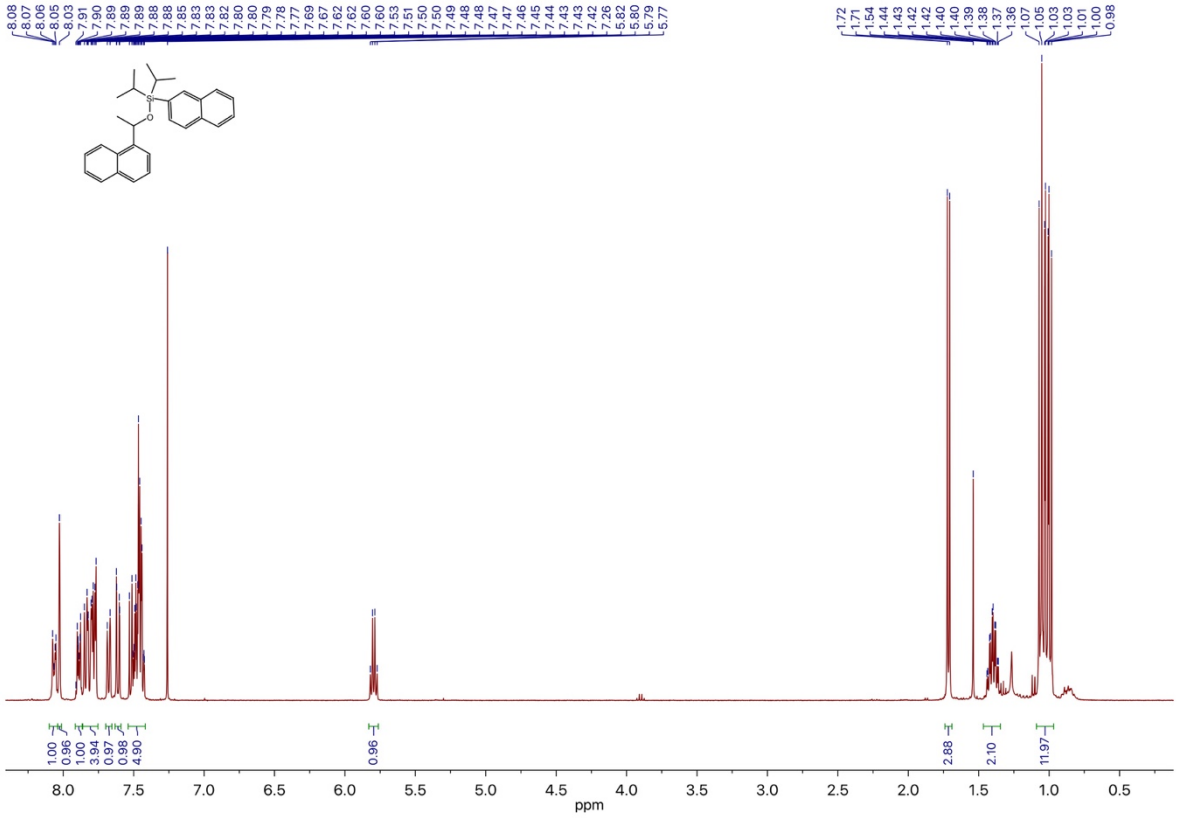


Figure S60: ^{1}H NMR spectrum of silyl ether **5bc** (400 MHz, $CDCl_3$).

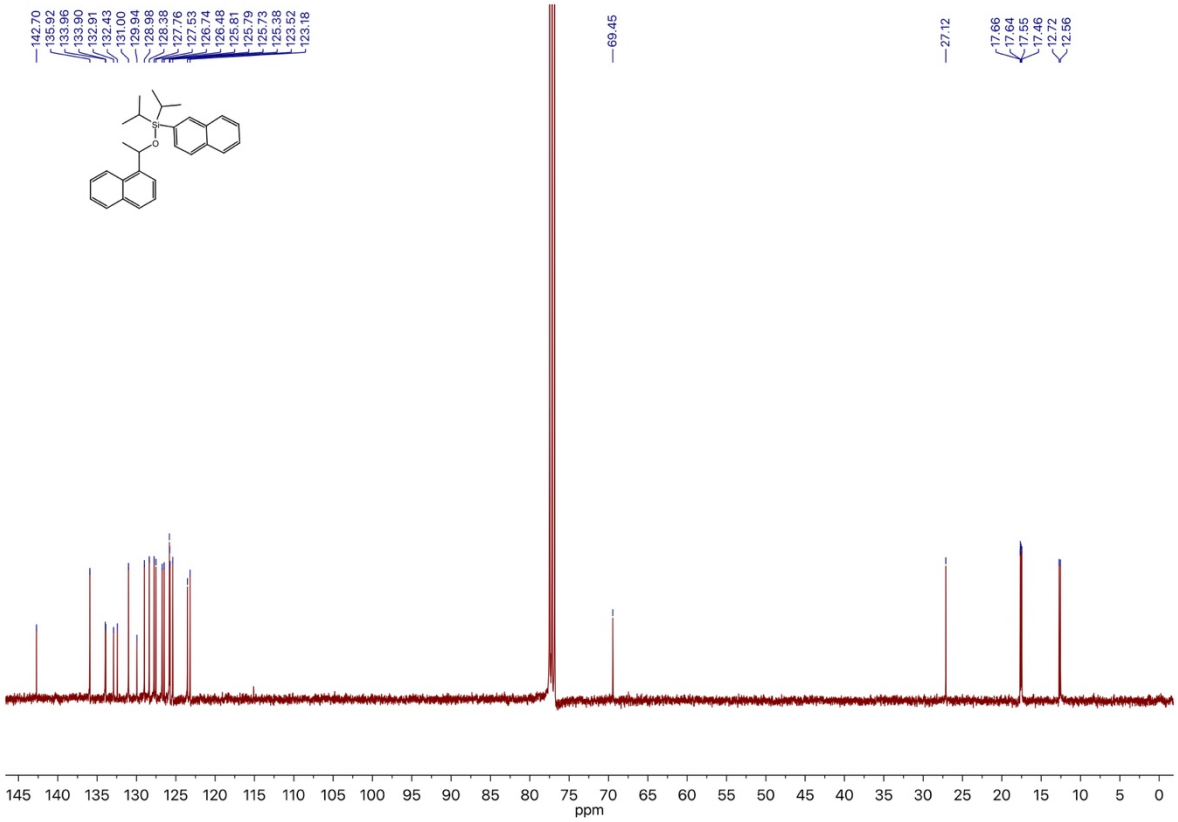


Figure S61: ^{13}C NMR spectrum of silyl ether **5bc** (101 MHz, $CDCl_3$).

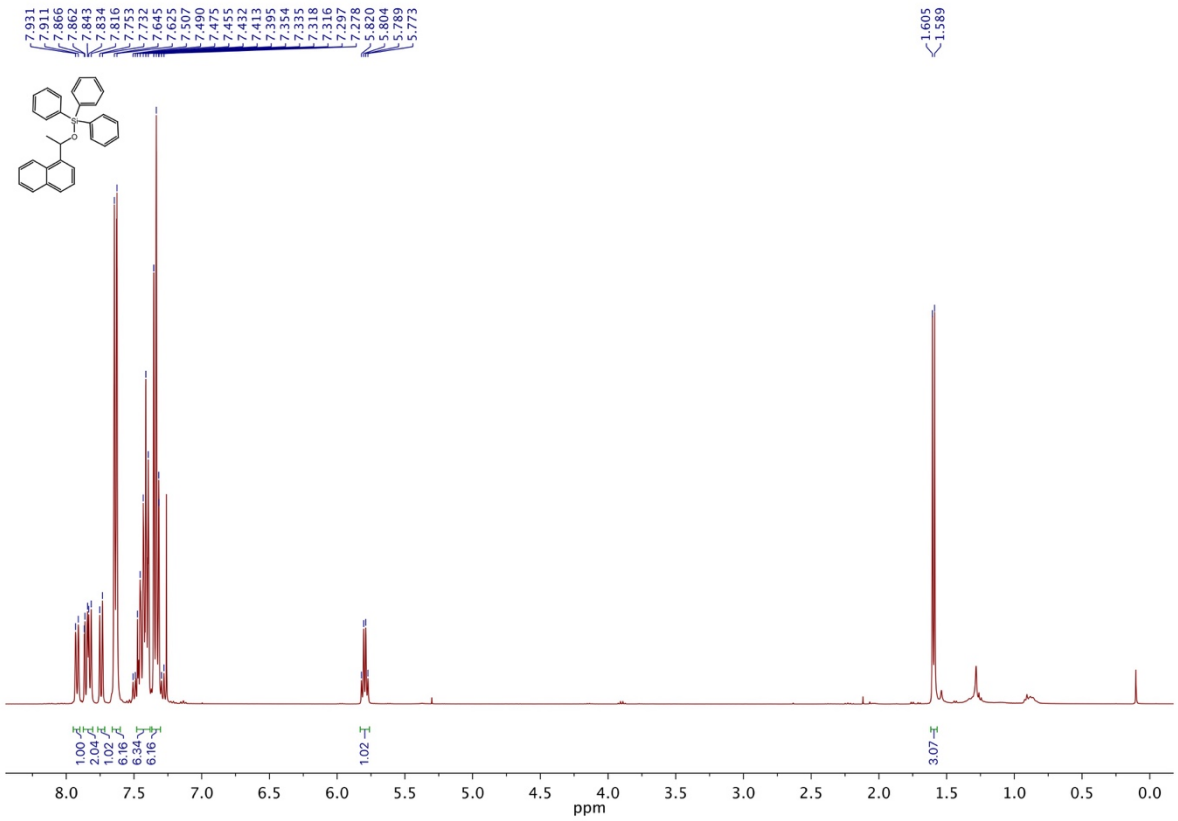


Figure S62: ^{1}H NMR spectrum of silyl ether **5bd** (400 MHz, $CDCl_3$).

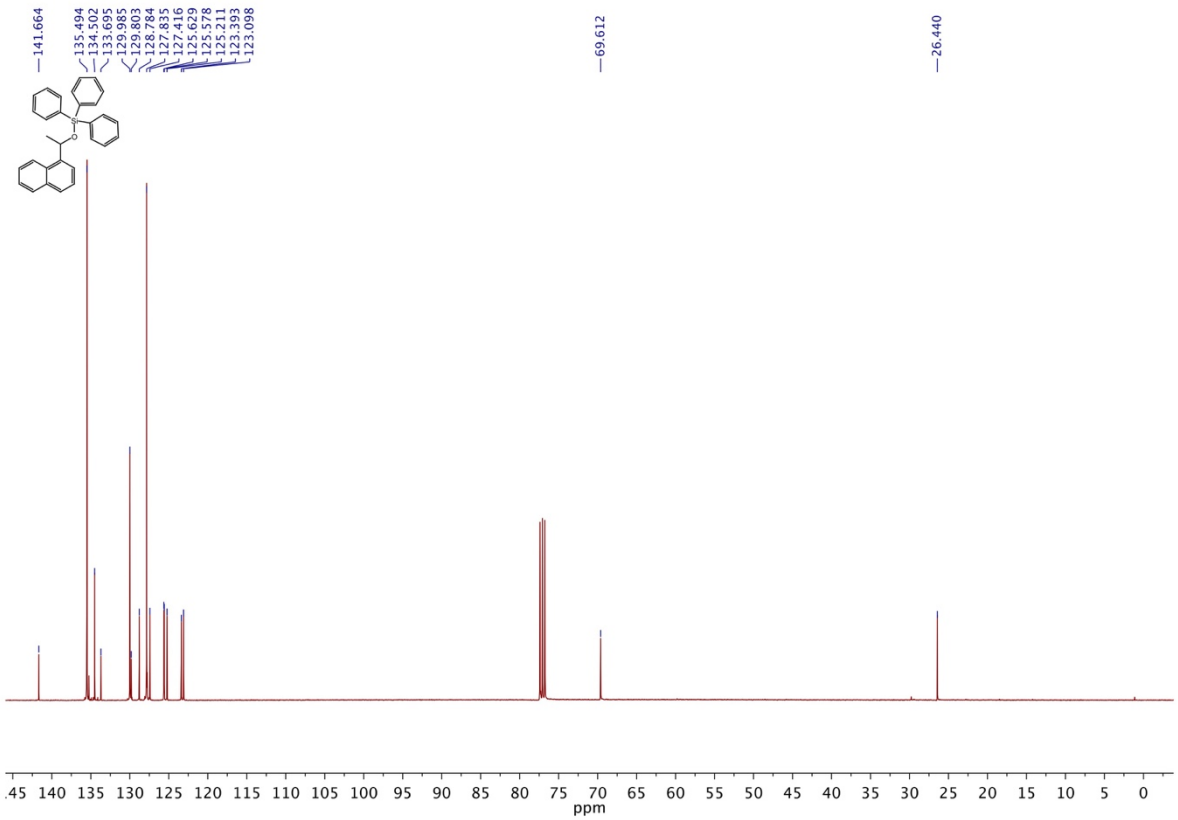


Figure S63: ^{13}C NMR spectrum of silyl ether **5bd** (101 MHz, $CDCl_3$).

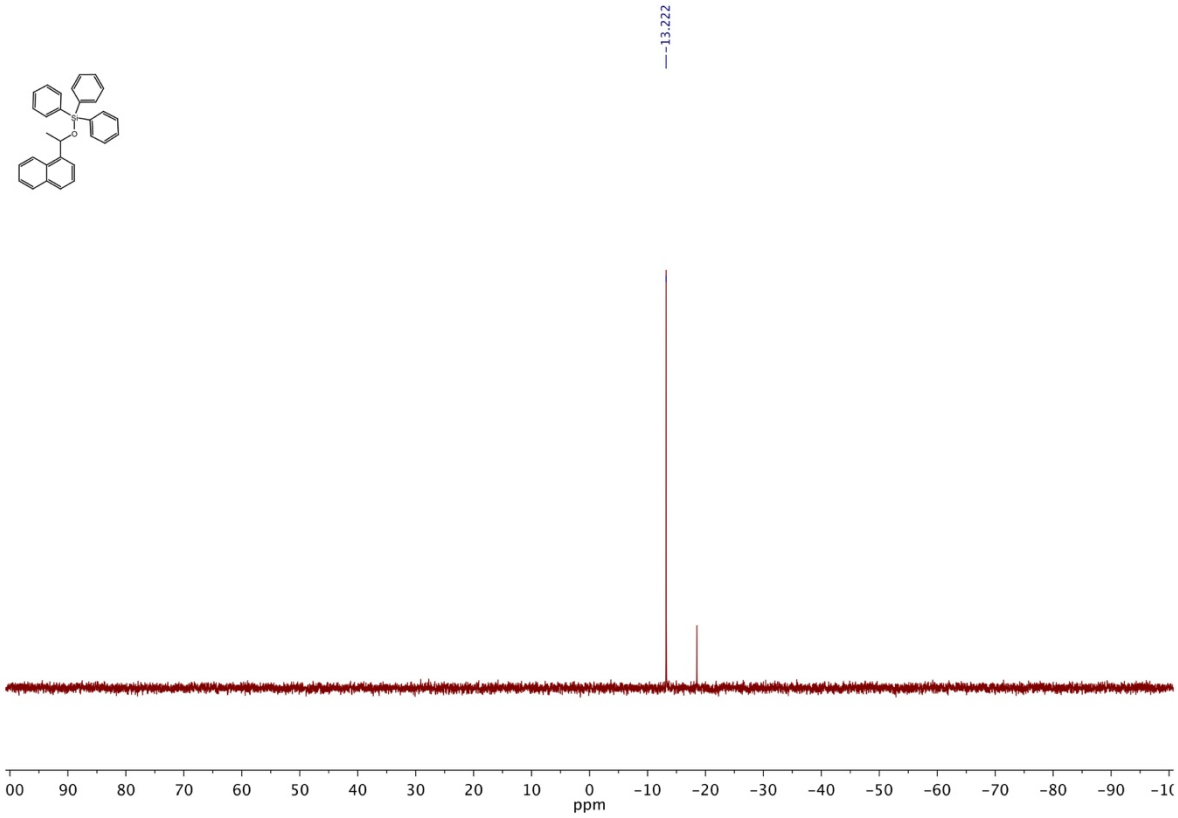


Figure S64: ^{29}Si NMR spectrum of silyl ether **5bd** (79 MHz, $CDCl_3$).

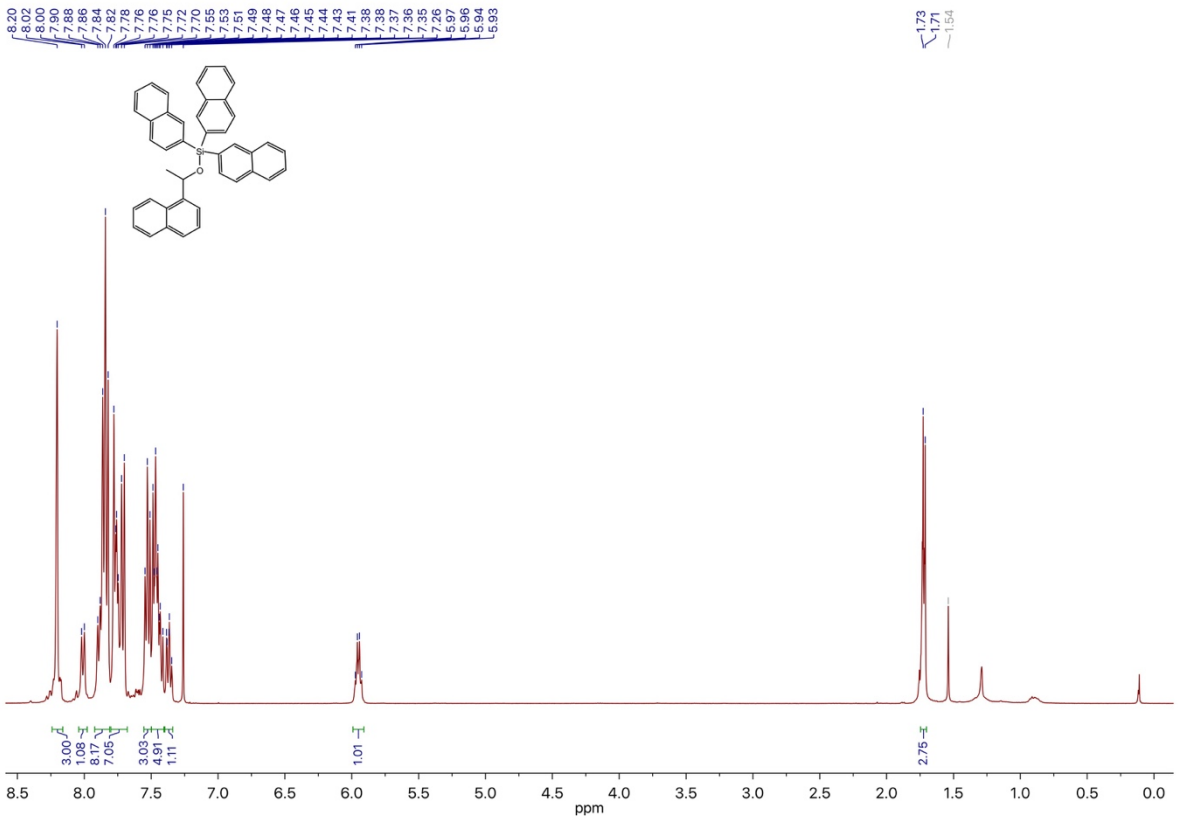


Figure S65: ^{1}H NMR spectrum of silyl ether **5be** (400 MHz, $CDCl_3$).

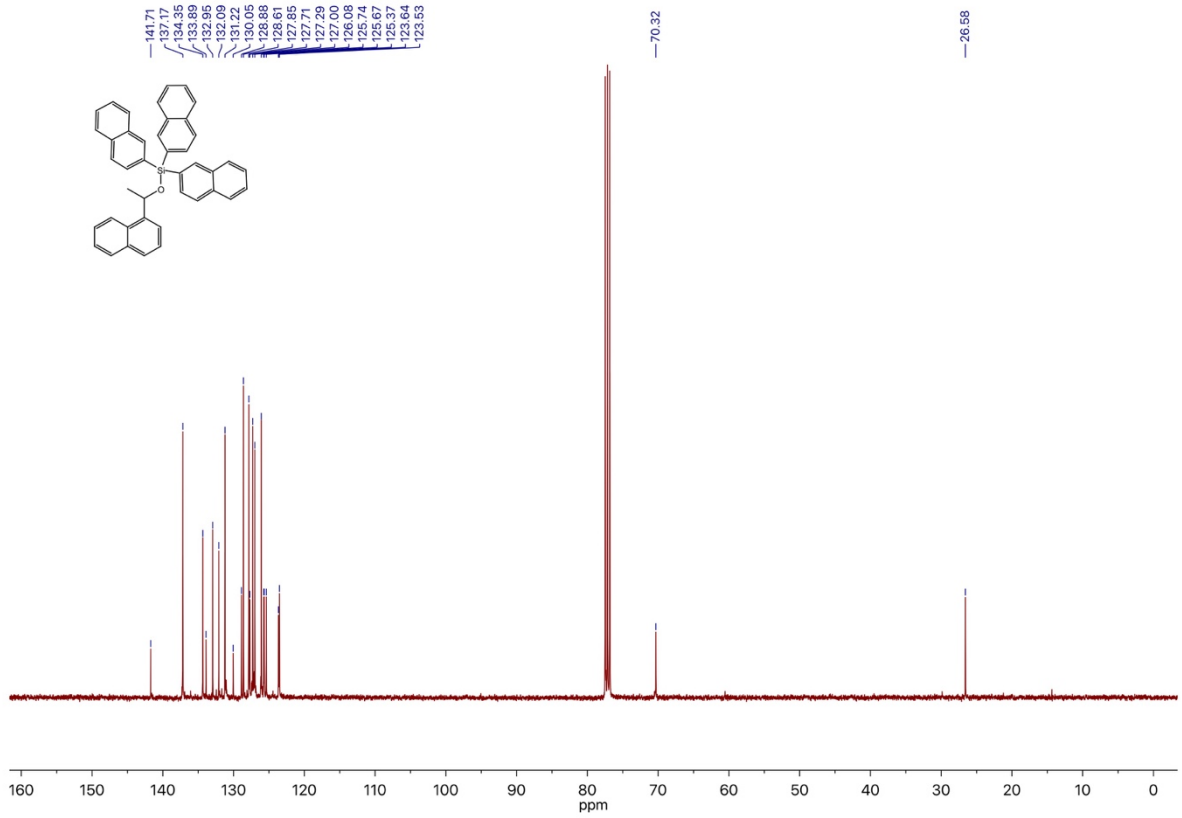


Figure S66: ^{13}C NMR spectrum of silyl ether **5be** (101 MHz, $CDCl_3$).

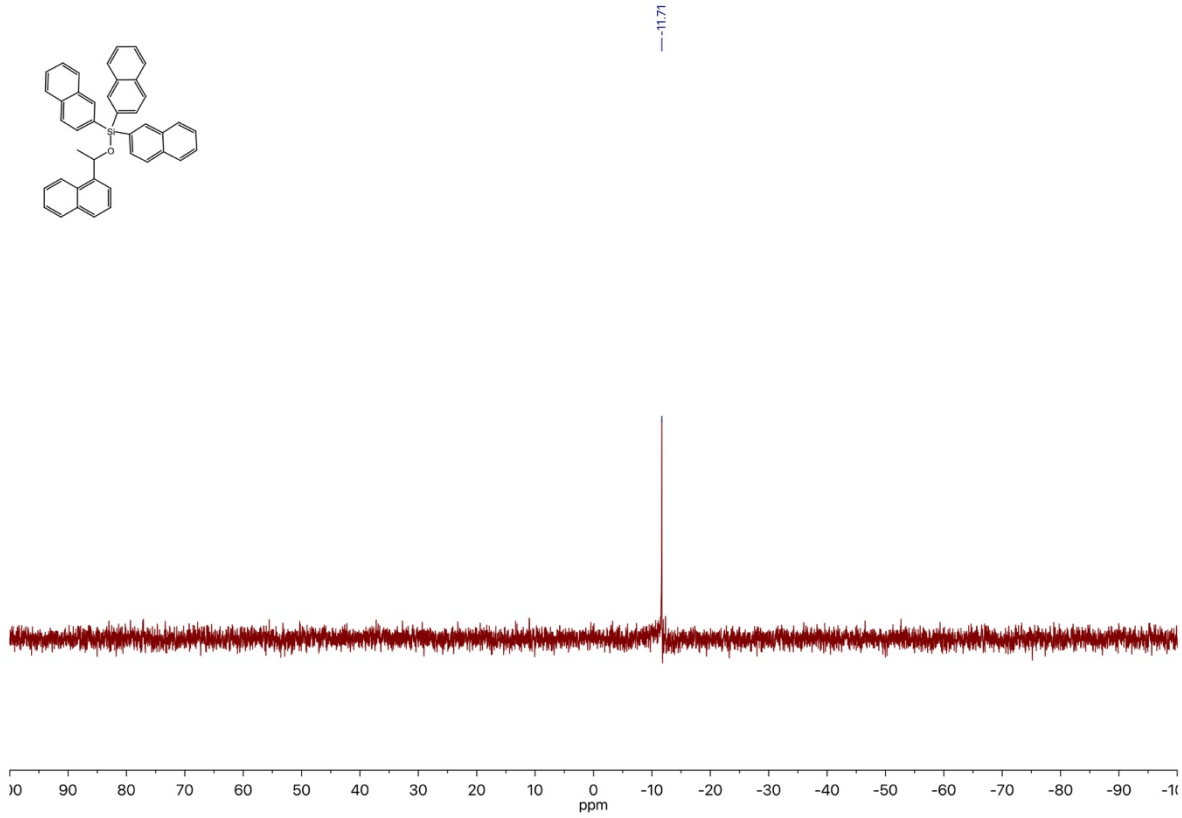


Figure S67: ^{29}Si NMR spectrum of silyl ether **5be** (79 MHz, $CDCl_3$).

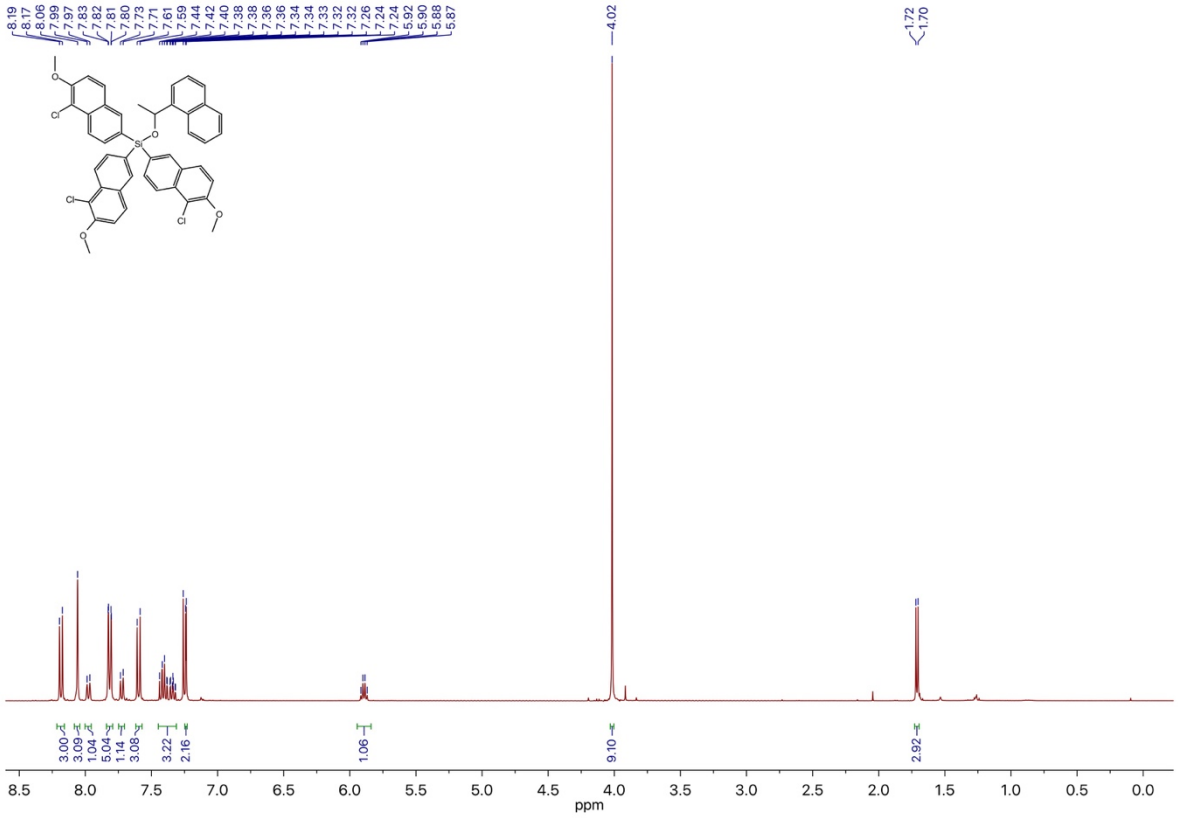


Figure S68: ^{1}H NMR spectrum of silyl ether **5bf** (400 MHz, $CDCl_3$).

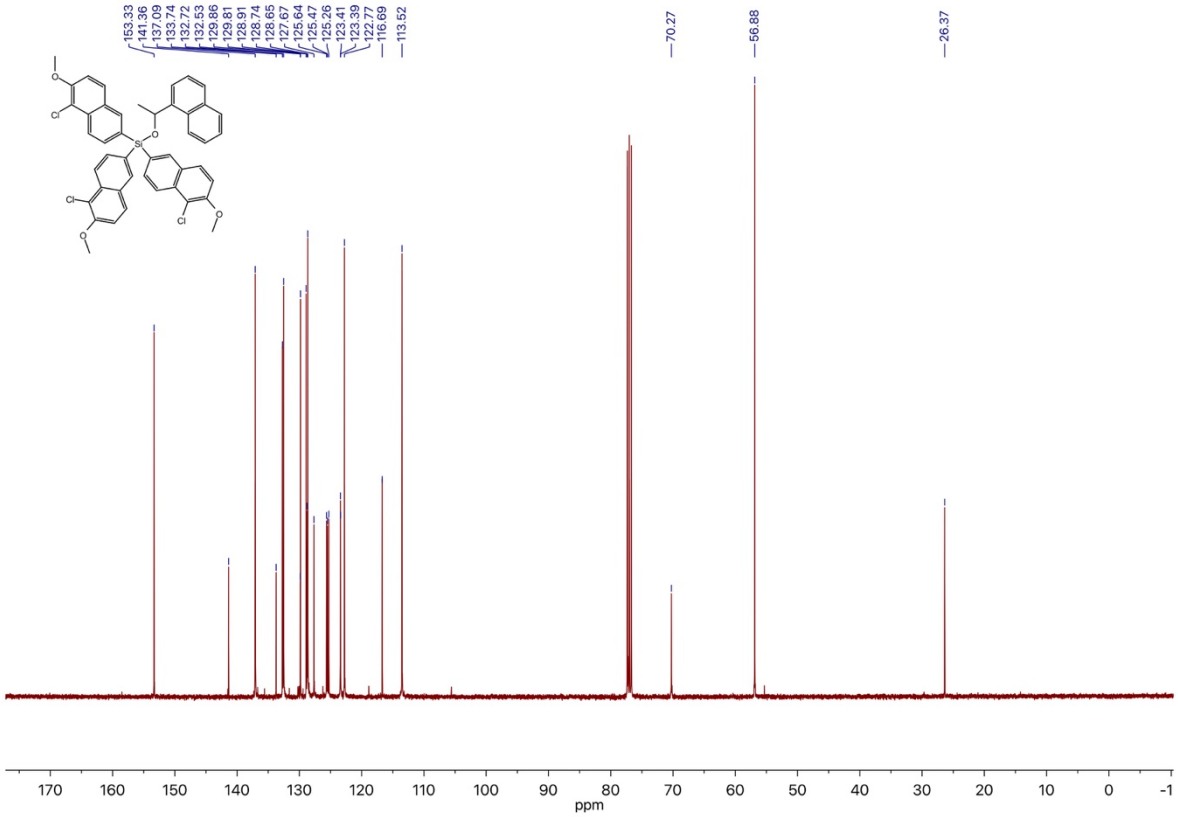


Figure S69: ^{13}C NMR spectrum of silyl ether **5bf** (101 MHz, $CDCl_3$).

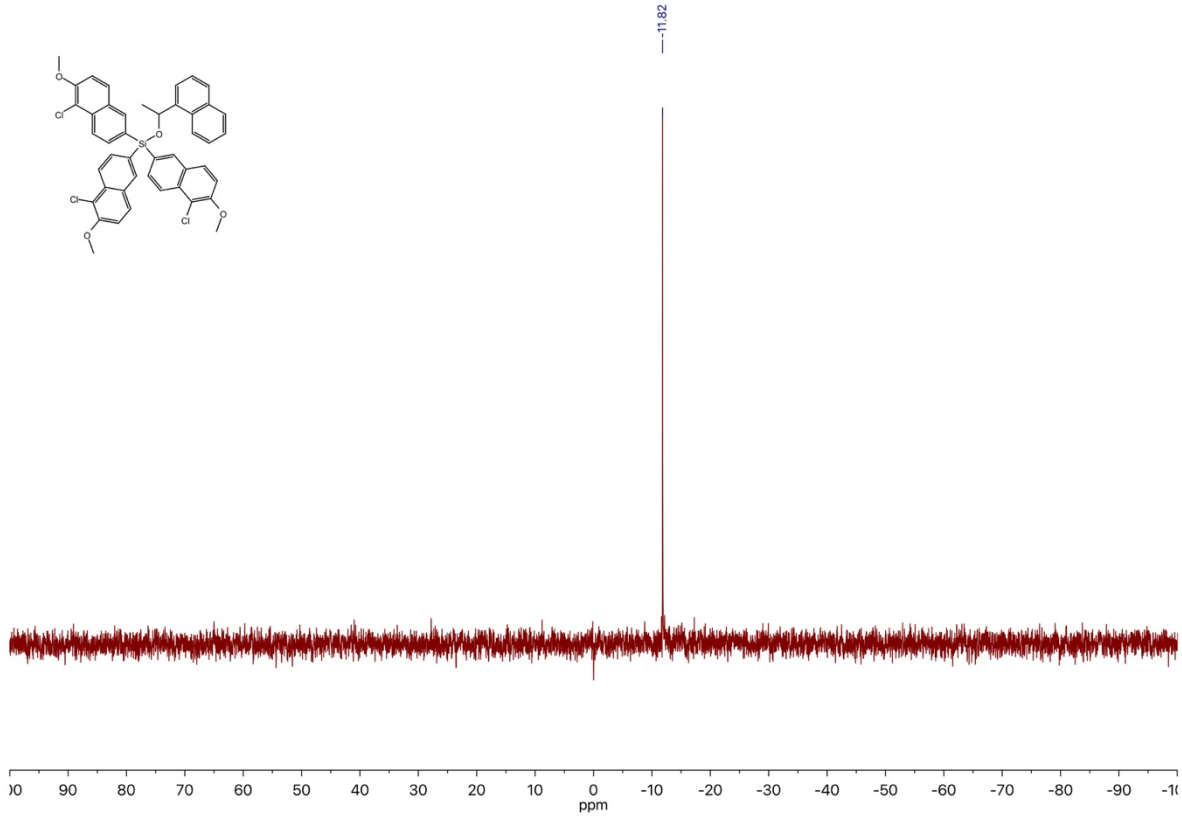


Figure S70: ^{29}Si NMR spectrum of silyl ether **5bf** (79 MHz, $CDCl_3$).

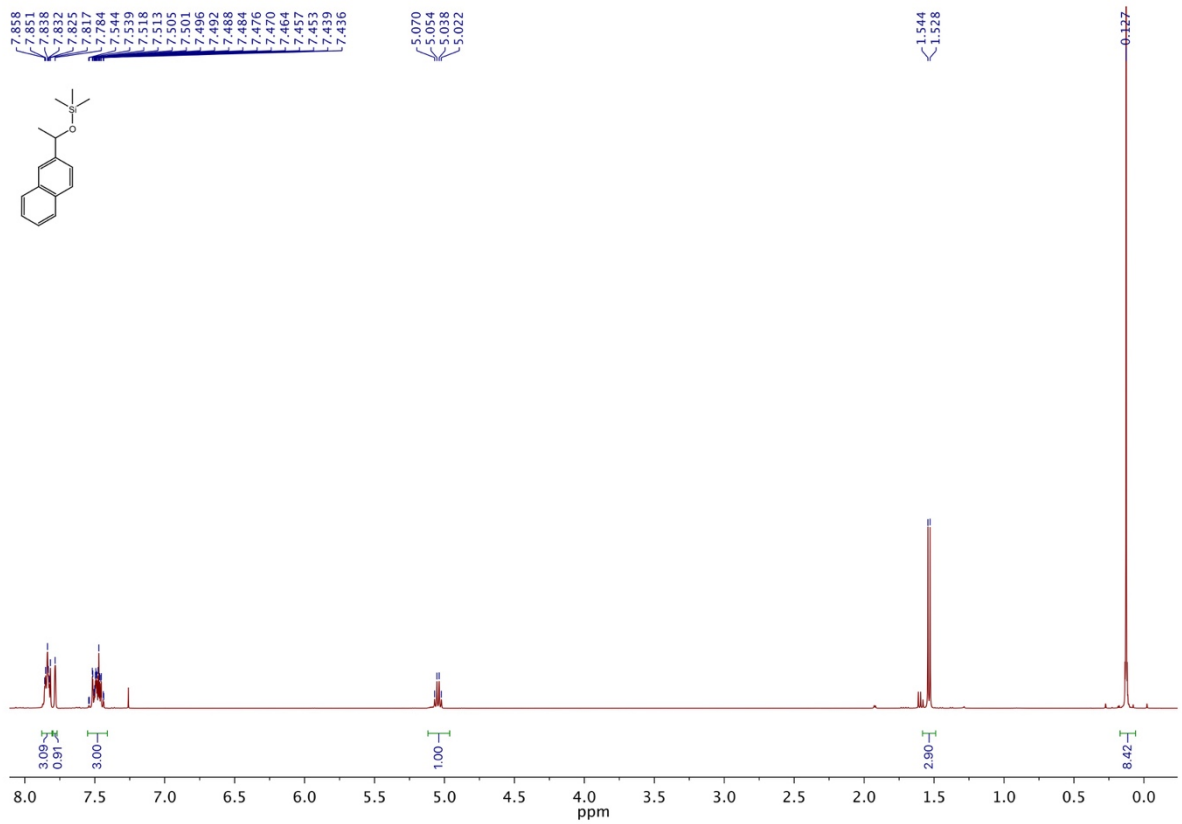


Figure S71: ^{1}H NMR spectrum of silyl ether **5ca** (400 MHz, $CDCl_3$).

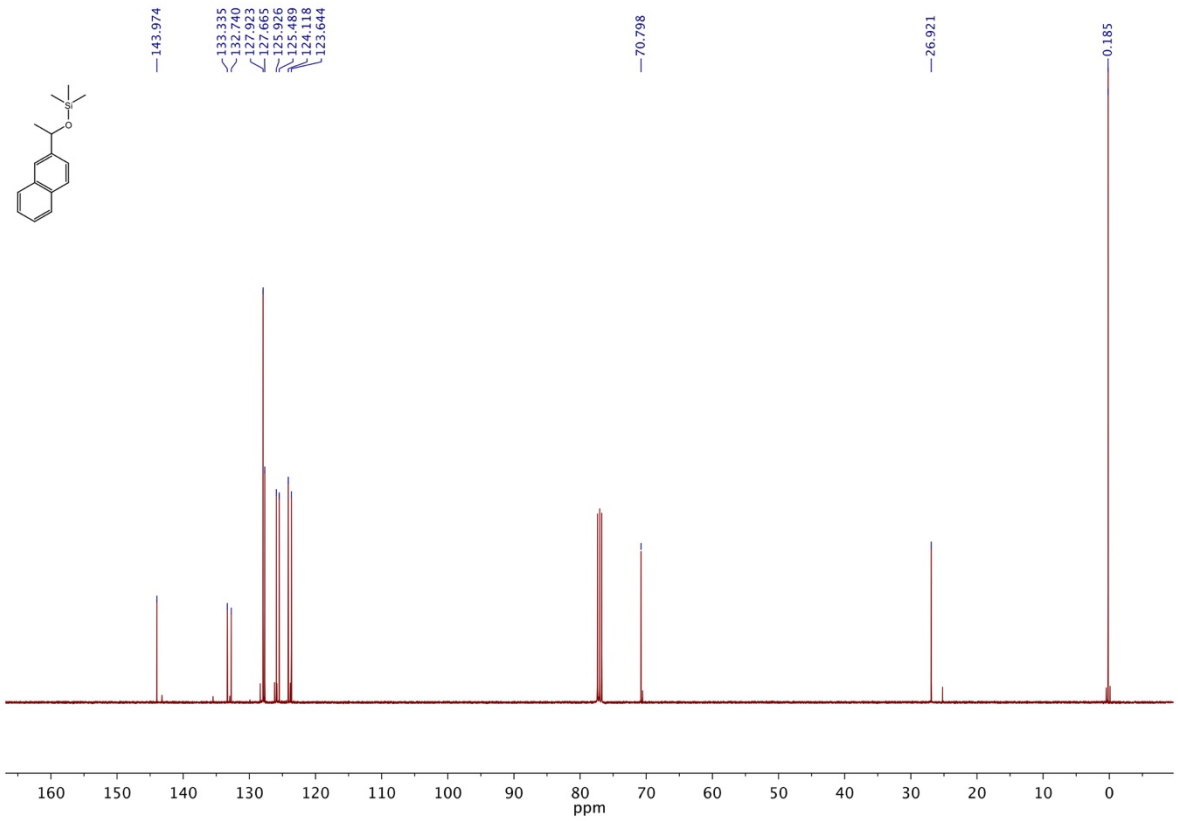


Figure S72: ^{13}C NMR spectrum of silyl ether **5ca** (101 MHz, $CDCl_3$).

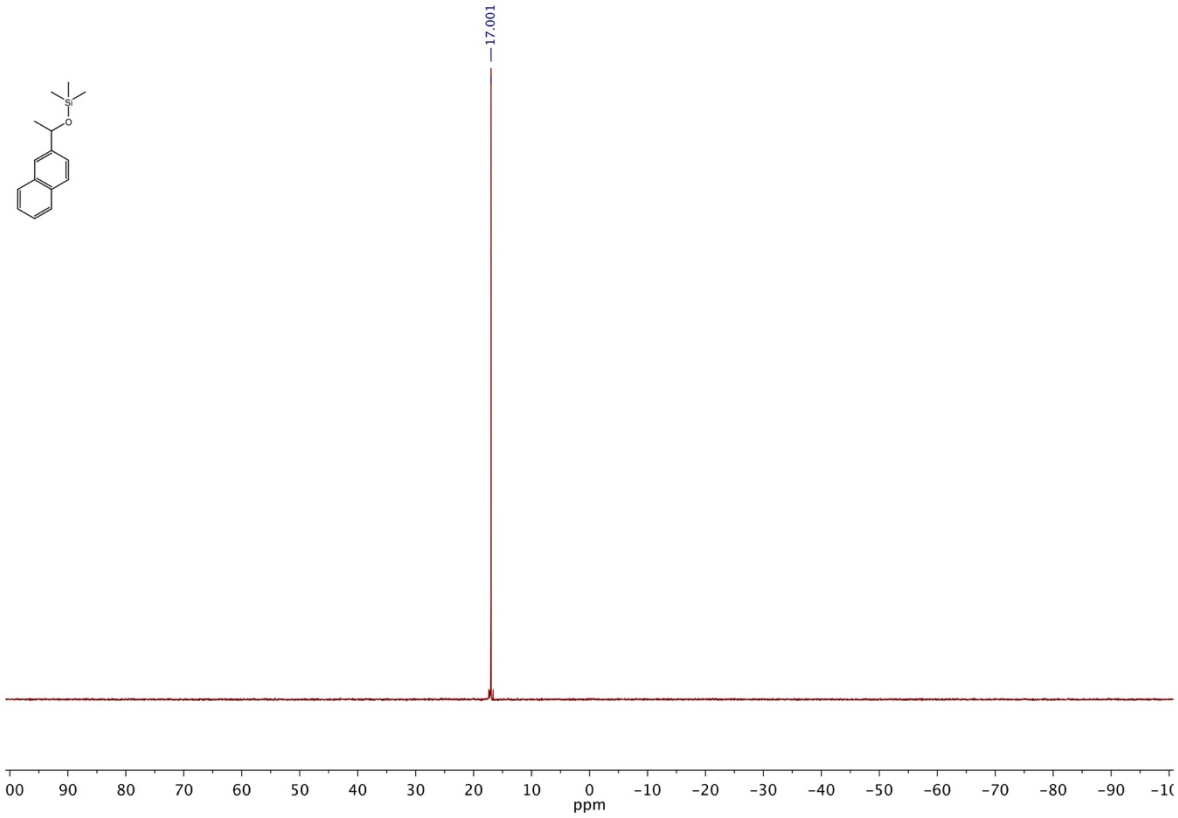


Figure S73: ^{29}Si NMR spectrum of silyl ether **5ca** (79 MHz, $CDCl_3$).

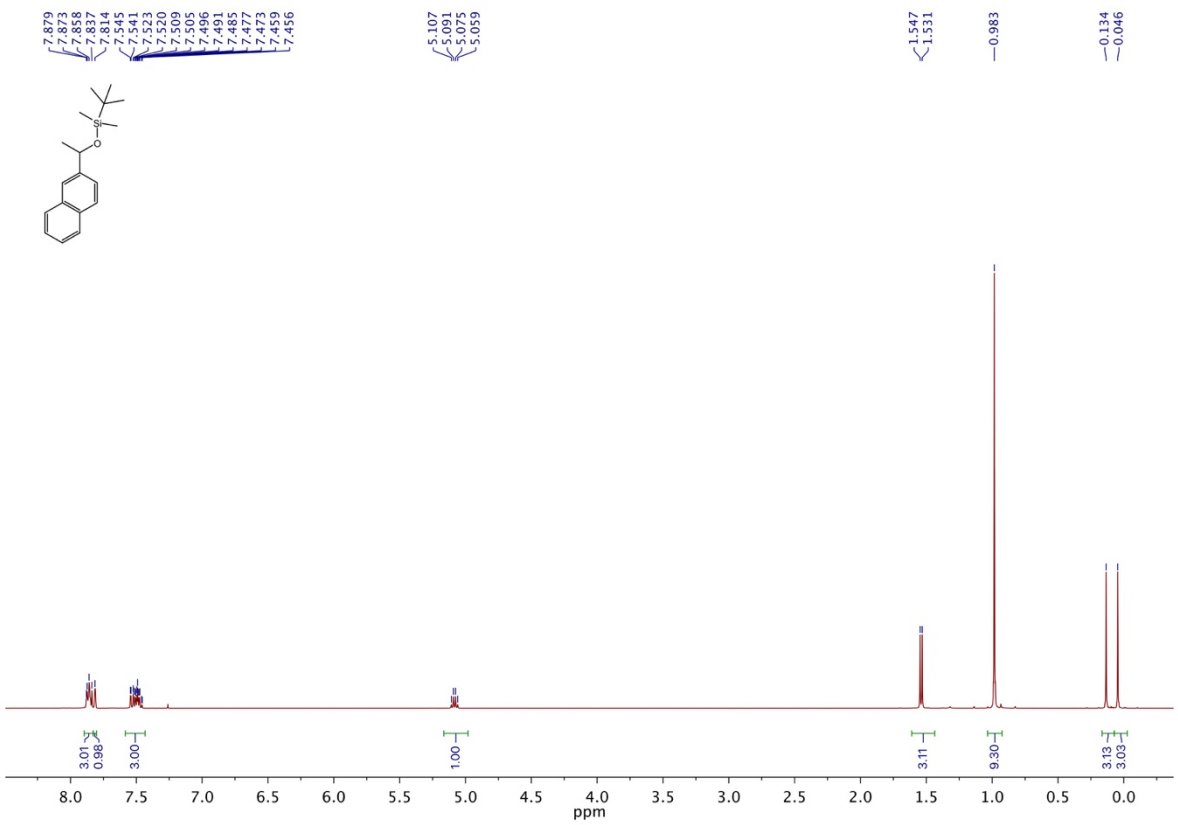


Figure S74: ^{1}H NMR spectrum of silyl ether **5cb** (400 MHz, $CDCl_3$).

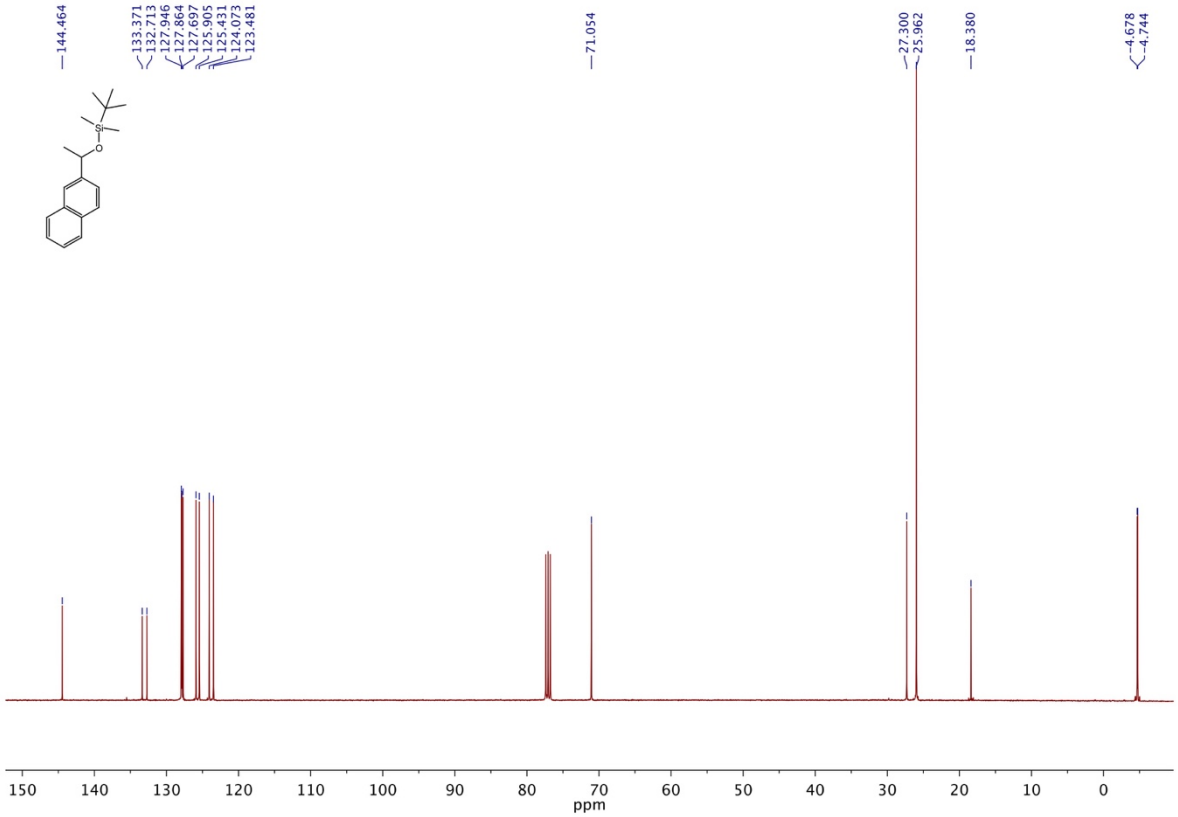


Figure S75: ^{13}C NMR spectrum of silyl ether **5cb** (101 MHz, $CDCl_3$).

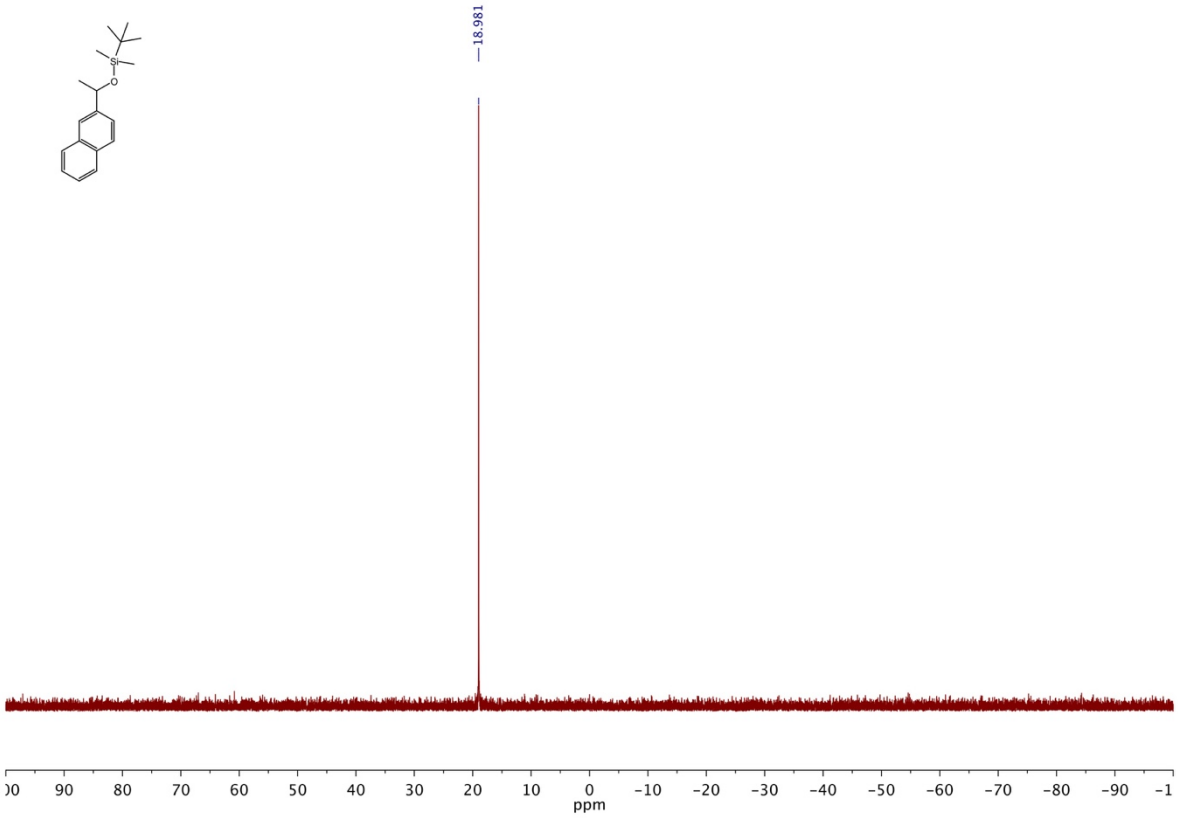


Figure S76: ^{29}Si NMR spectrum of silyl ether **5cb** (79 MHz, $CDCl_3$).

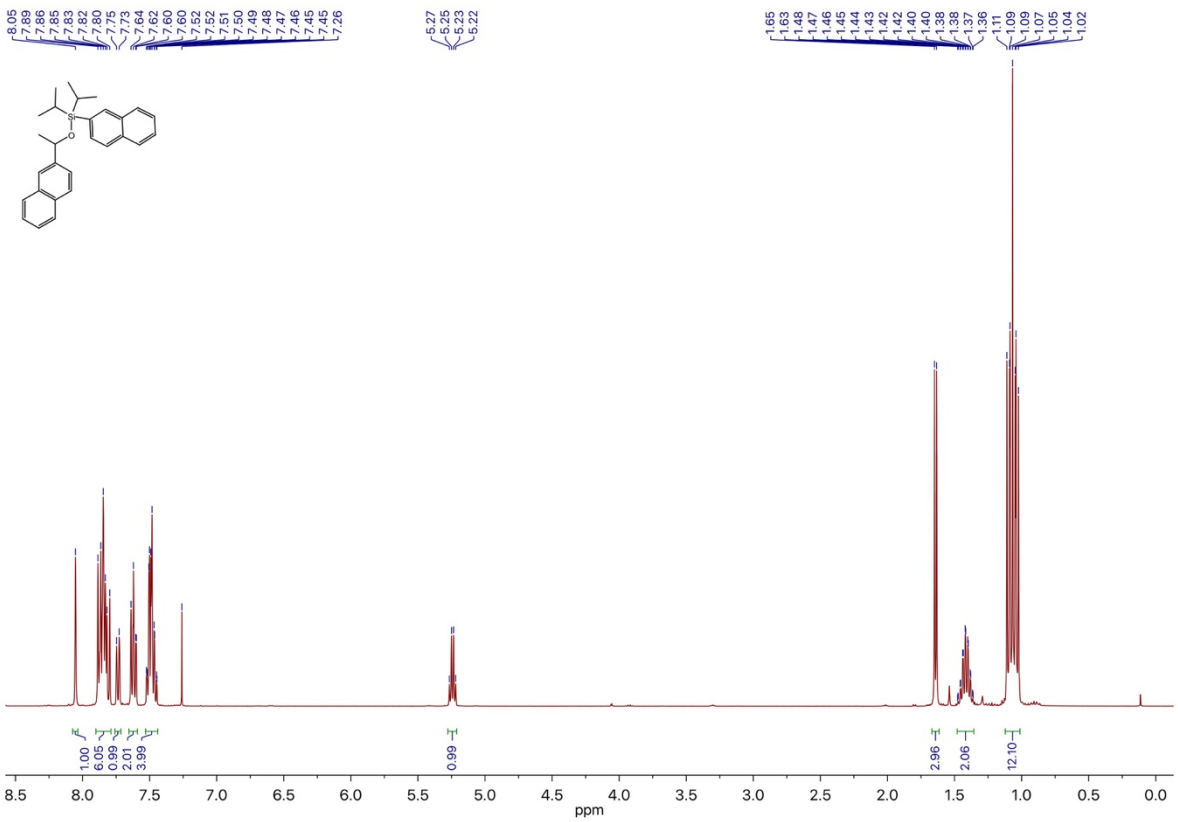


Figure S77: ^{1}H NMR spectrum of silyl ether **5cc** (400 MHz, $CDCl_3$).

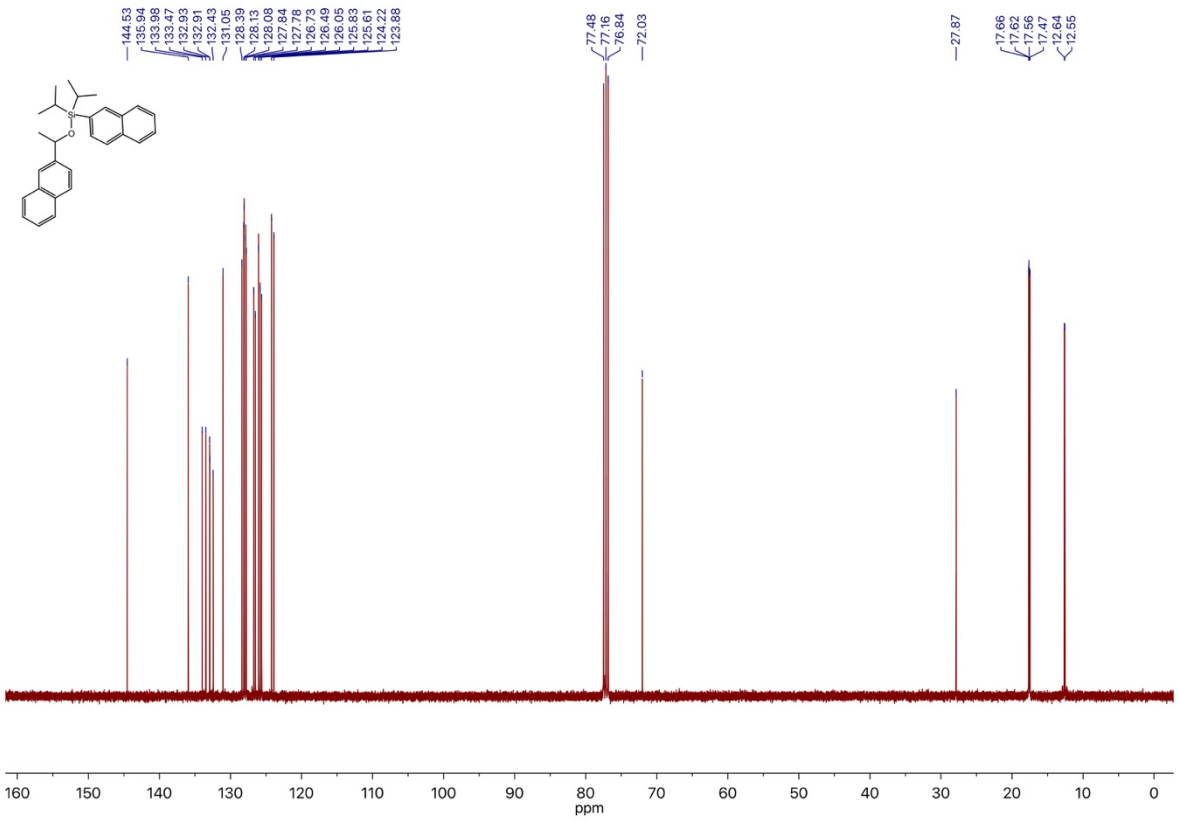


Figure S78: ^{13}C NMR spectrum of silyl ether **5cc** (101 MHz, $CDCl_3$).

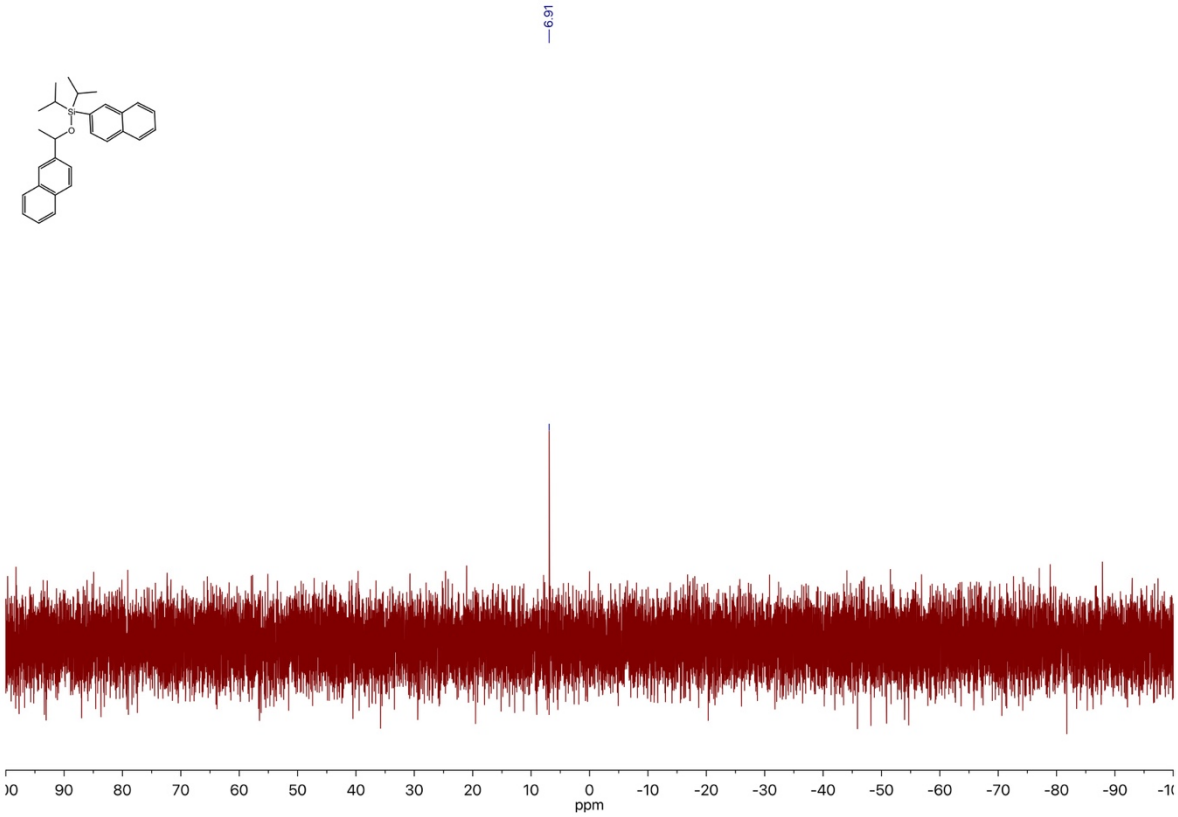


Figure S79: ^{29}Si NMR spectrum of silyl ether **5cc** (79 MHz, $CDCl_3$).

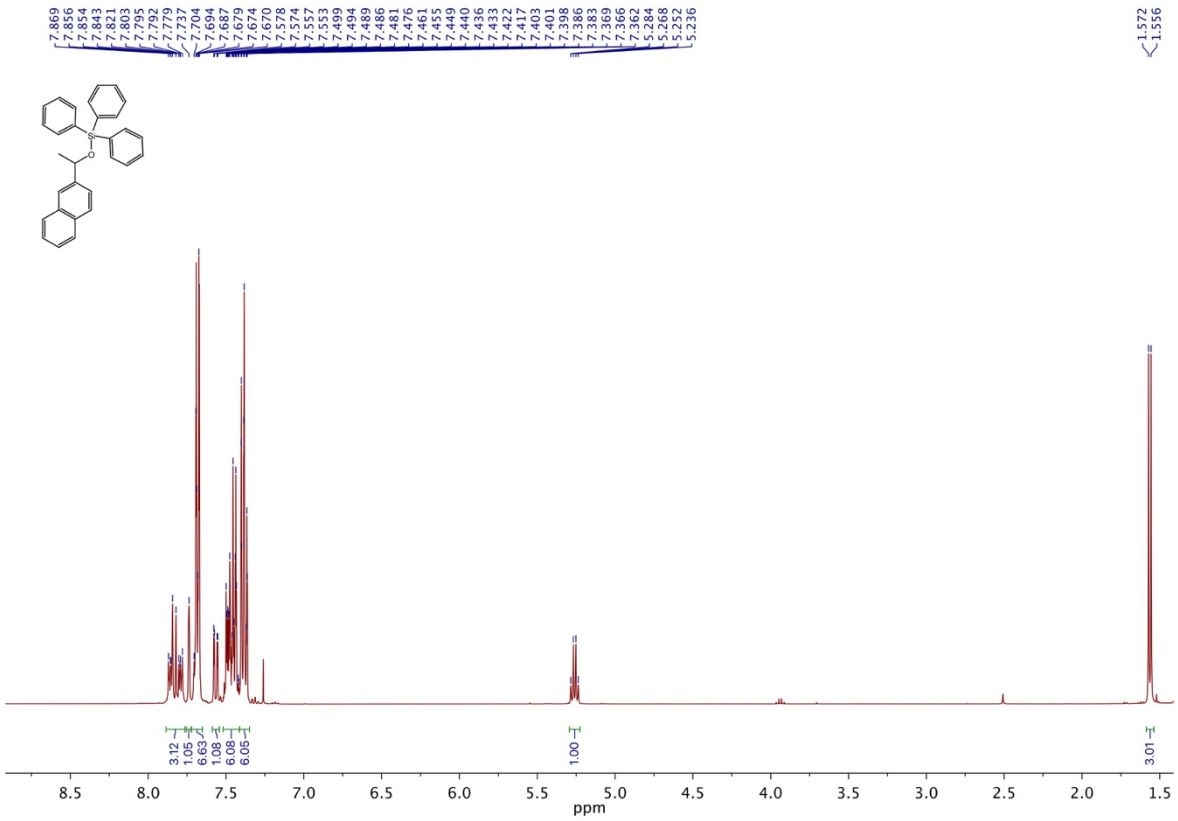


Figure S80: ^{1}H NMR spectrum of silyl ether **5cd** (400 MHz, $CDCl_3$).

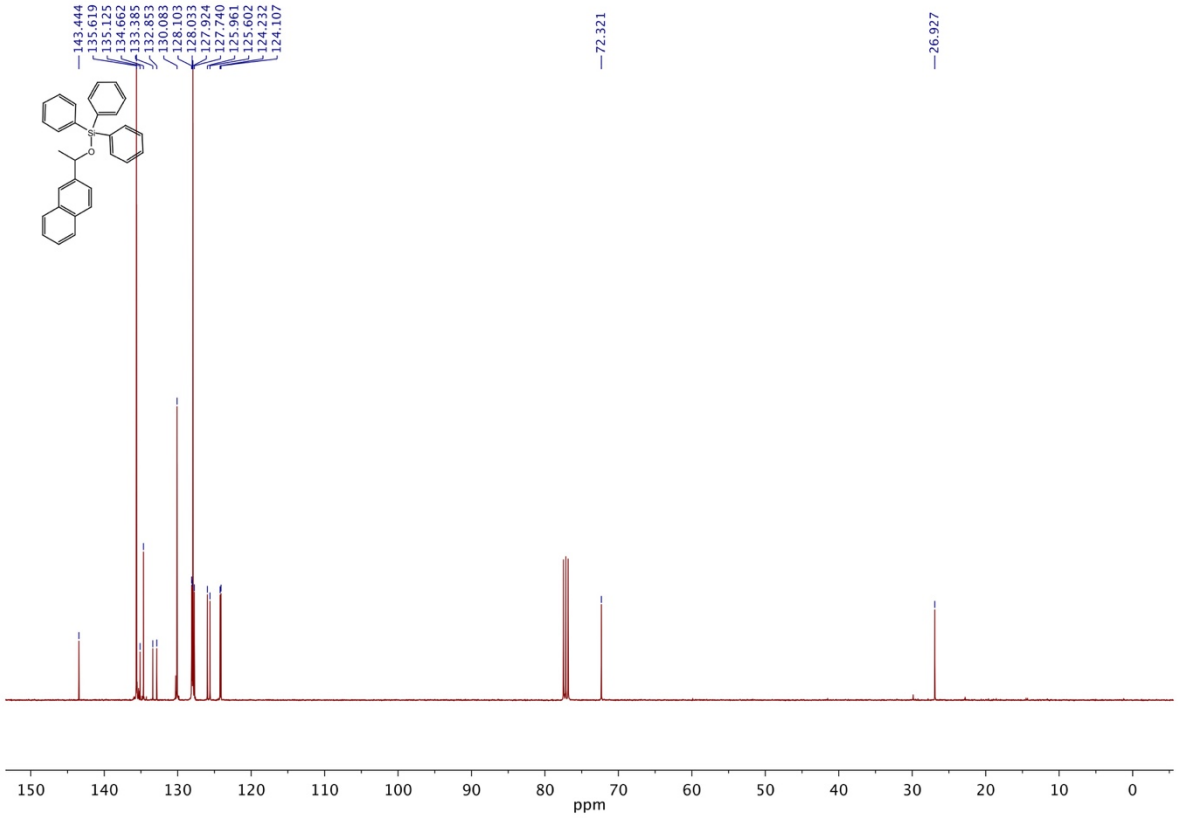


Figure S81: ^{13}C NMR spectrum of silyl ether **5cd** (101 MHz, $CDCl_3$).

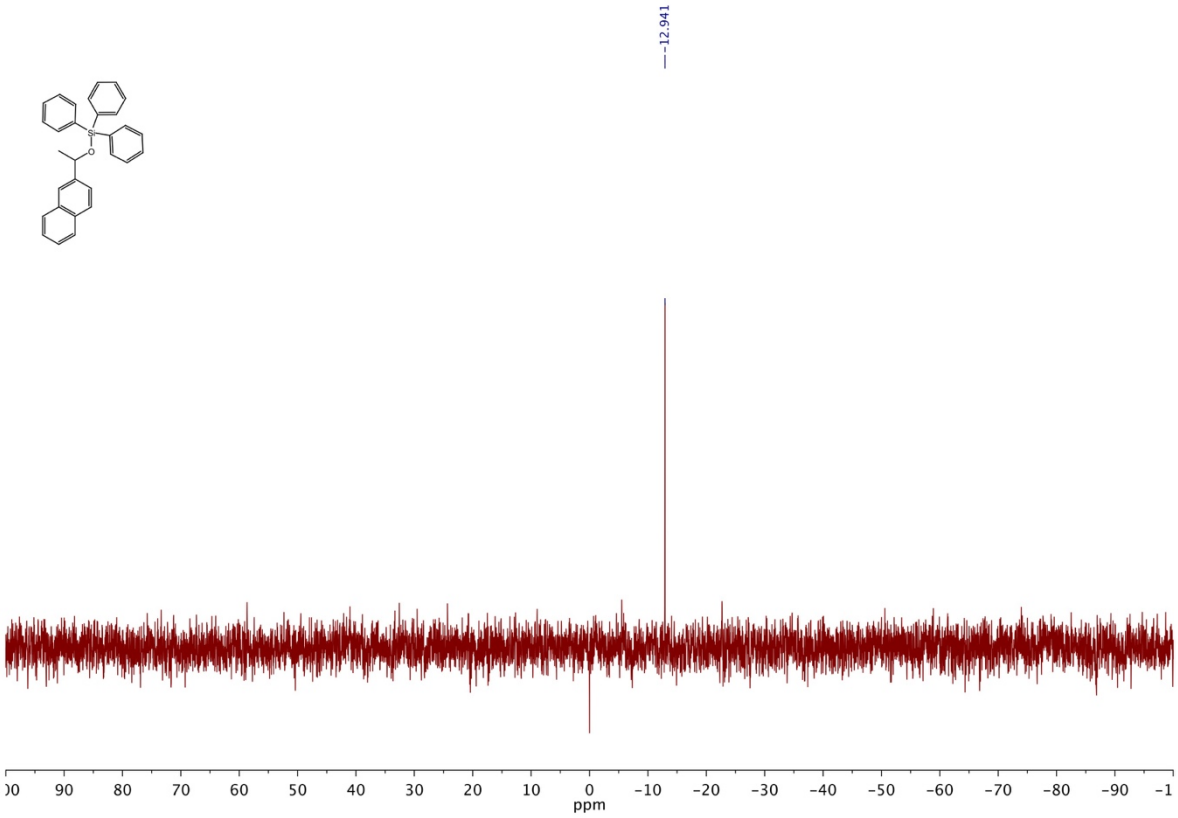


Figure S82: ^{29}Si NMR spectrum of silyl ether **5cd** (79 MHz, $CDCl_3$).

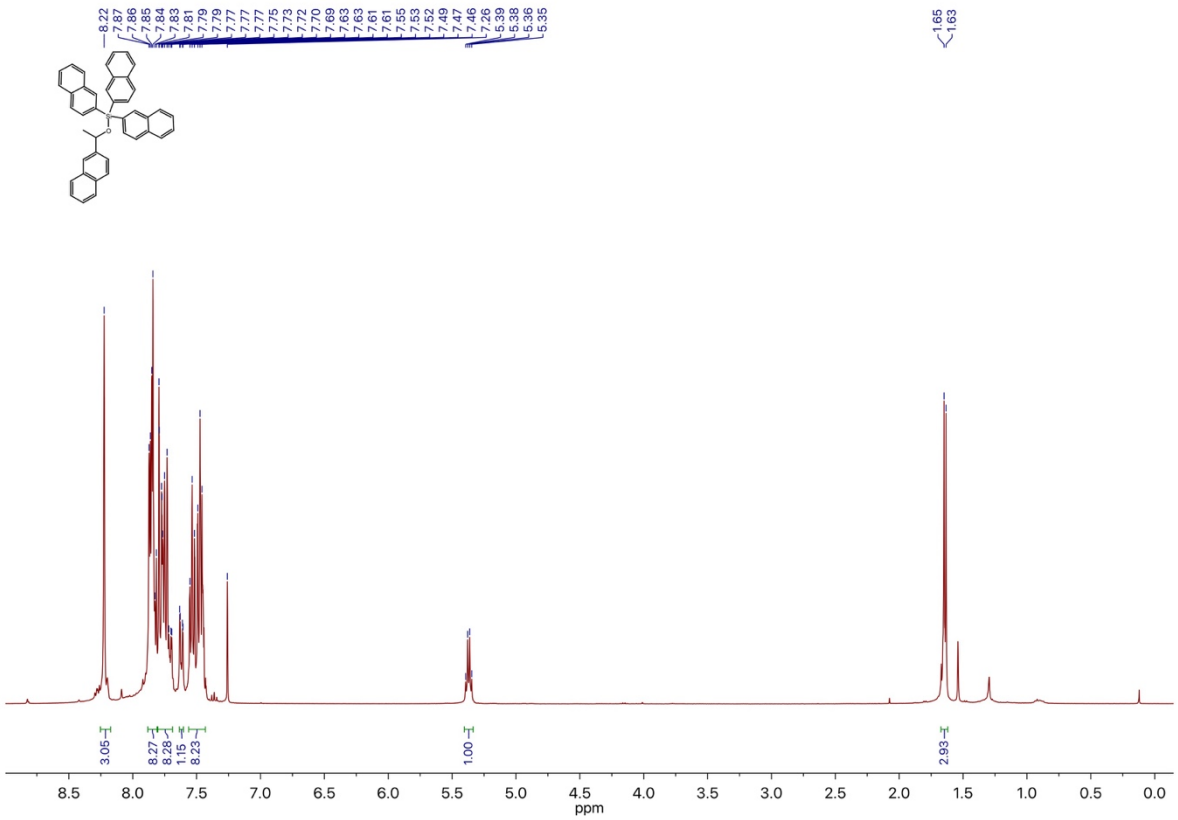


Figure S83: ^{1}H NMR spectrum of silyl ether **5ce** (400 MHz, $CDCl_3$).

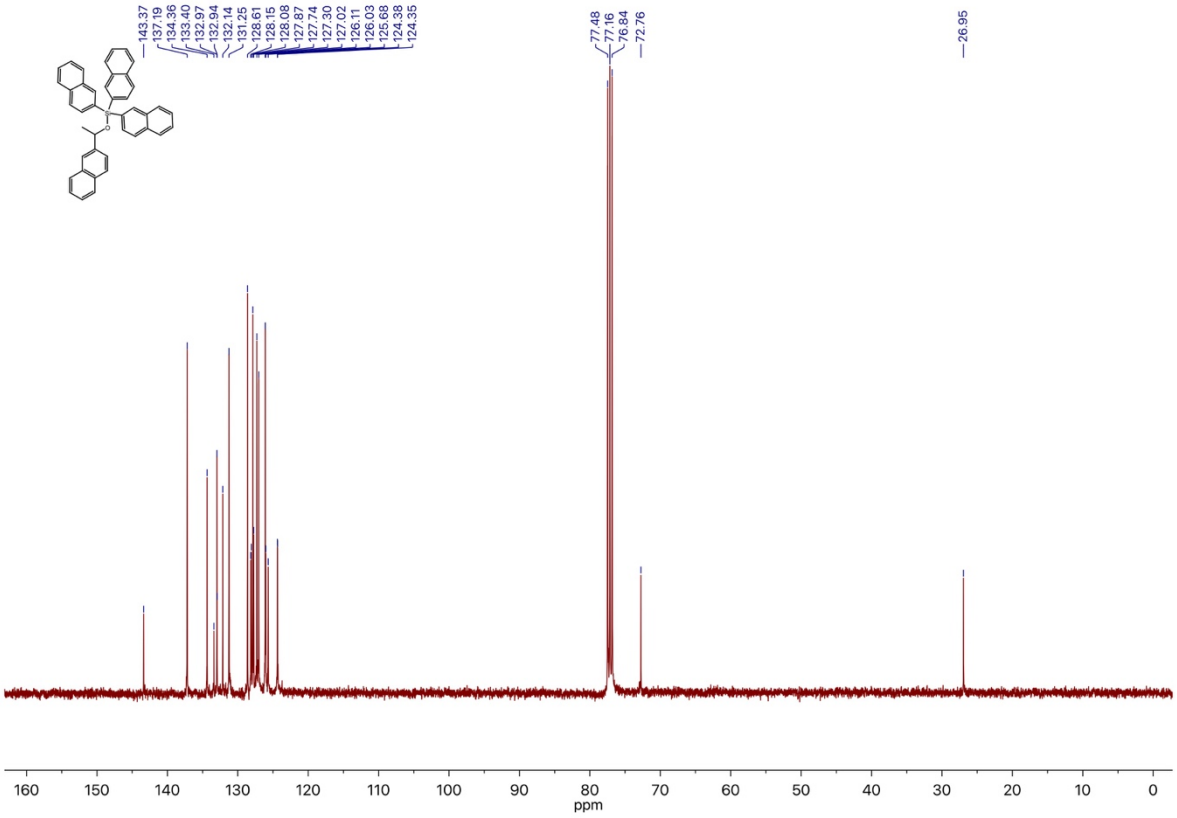


Figure S84: ^{13}C NMR spectrum of silyl ether **5ce** (101 MHz, $CDCl_3$).

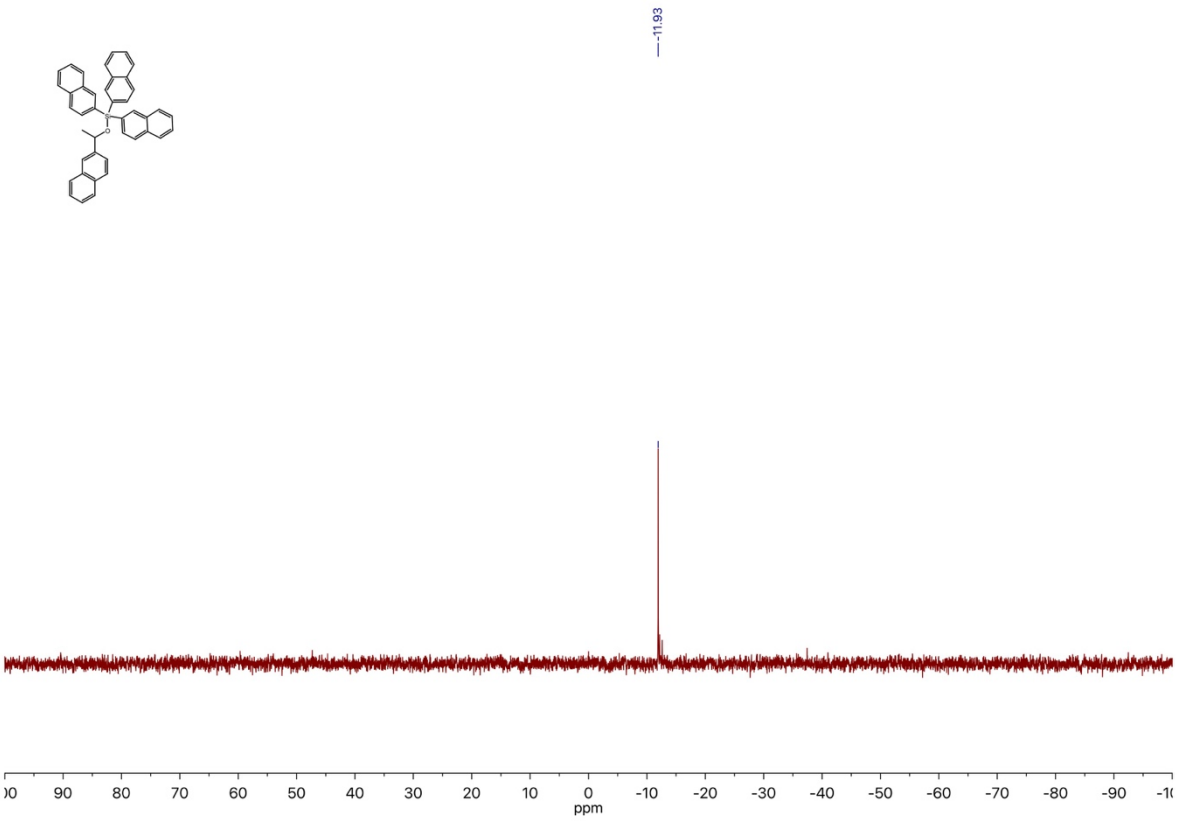


Figure S85: ^{29}Si NMR spectrum of silyl ether **5ce** (79 MHz, $CDCl_3$).

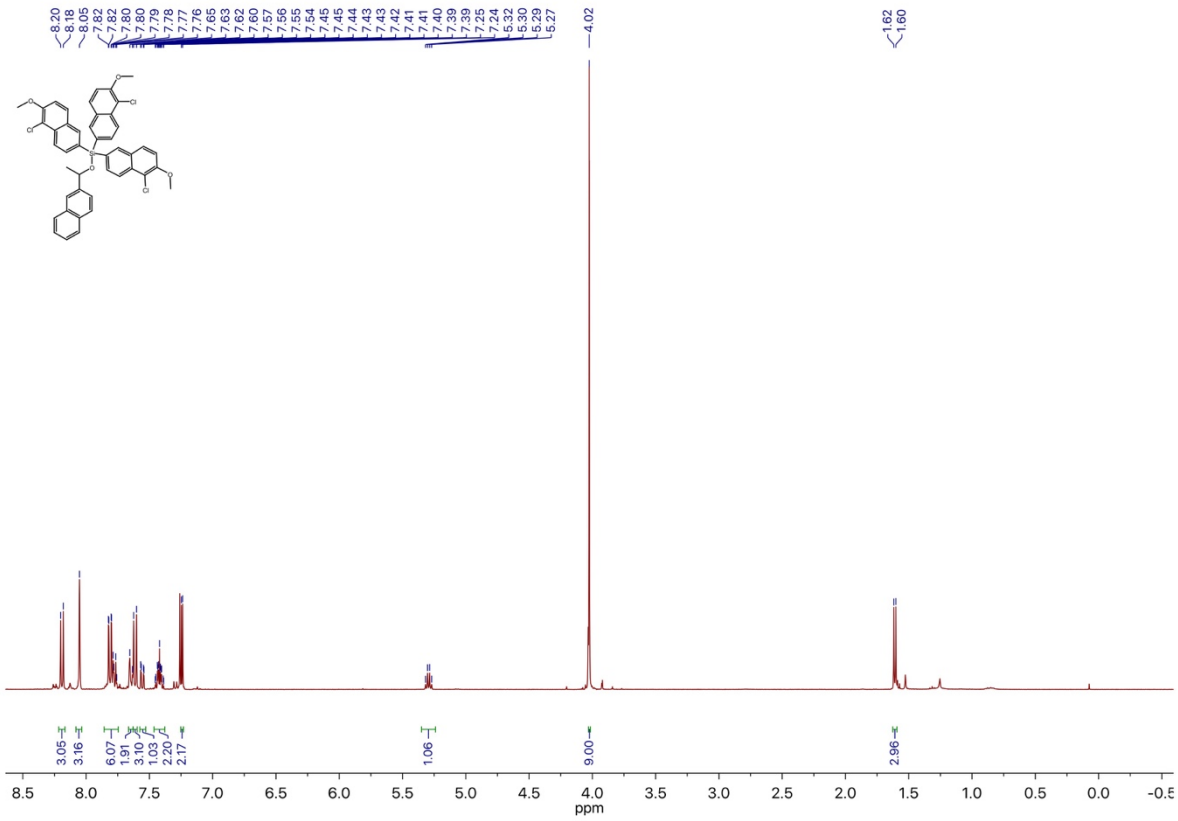


Figure S86: ^{1}H NMR spectrum of silyl ether **5cf** (400 MHz, $CDCl_3$).

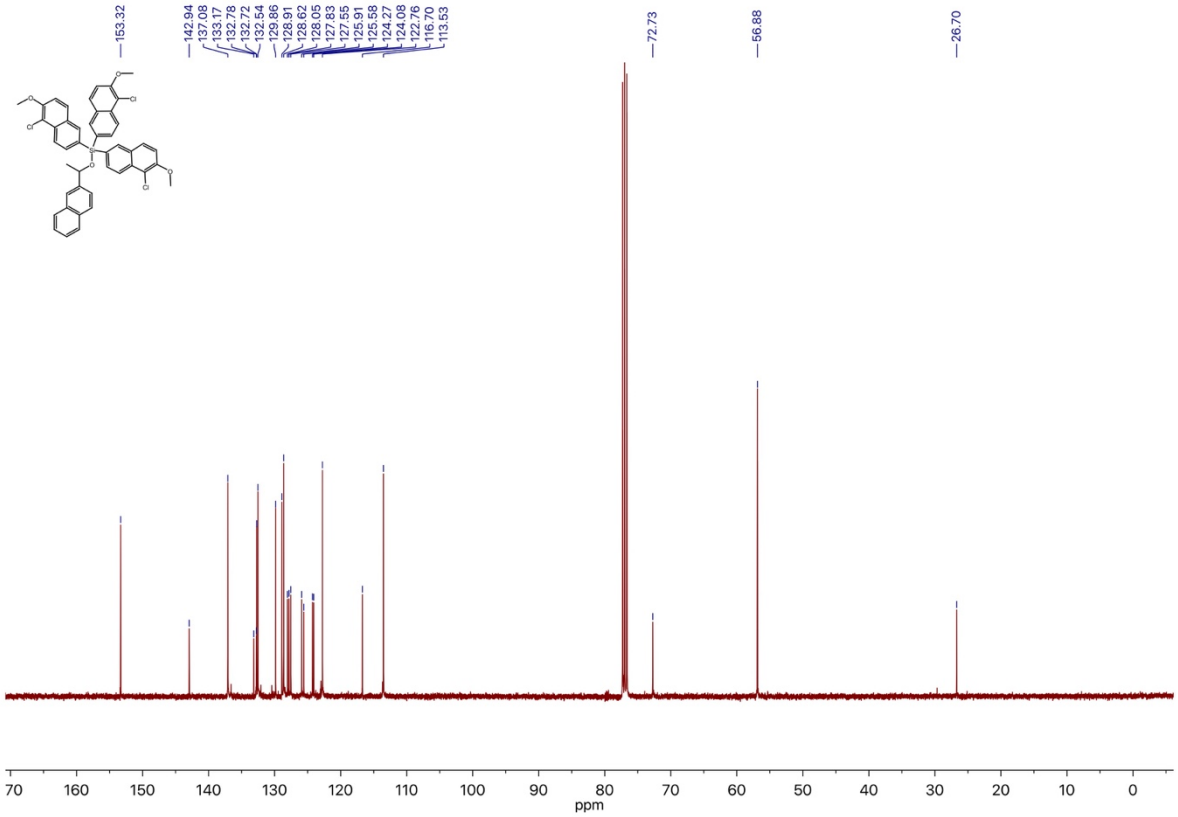


Figure S87: ^{13}C NMR spectrum of silyl ether **5cf** (101 MHz, $CDCl_3$).

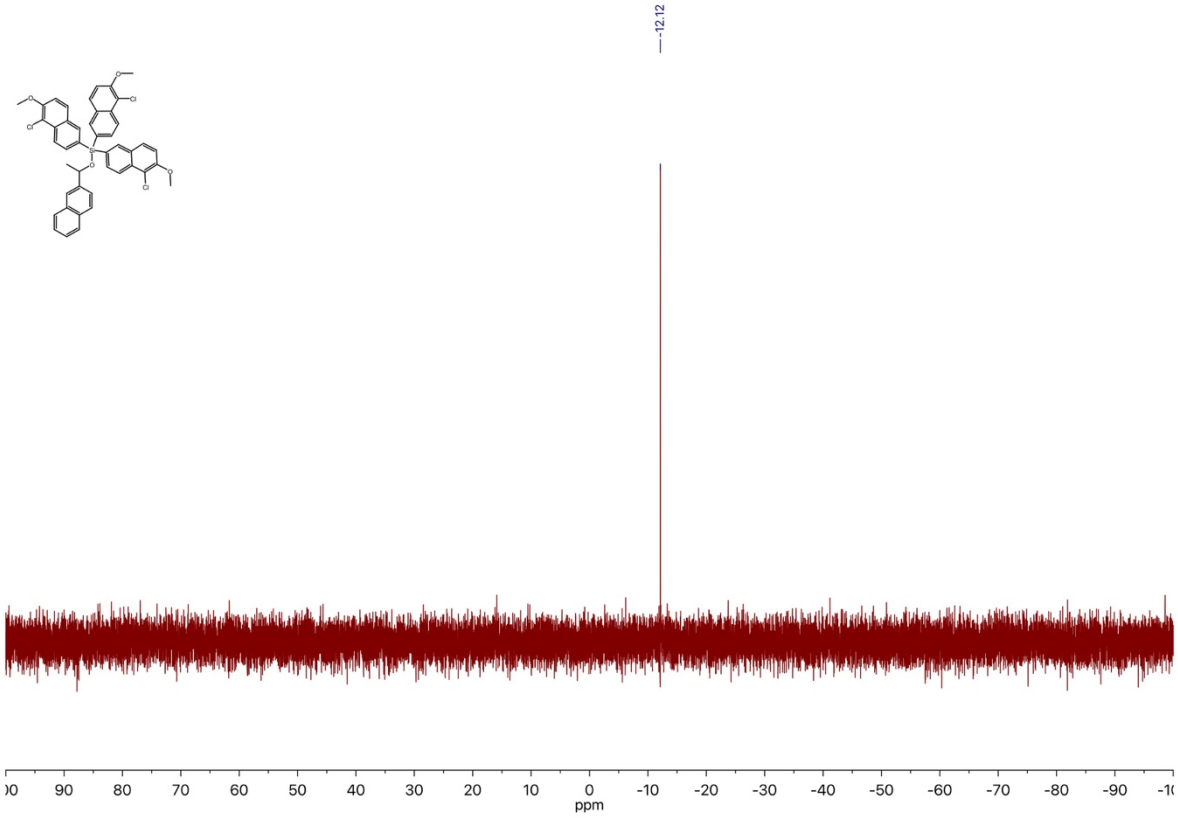


Figure S88: ^{29}Si NMR spectrum of silyl ether **5cf** (79 MHz, $CDCl_3$).

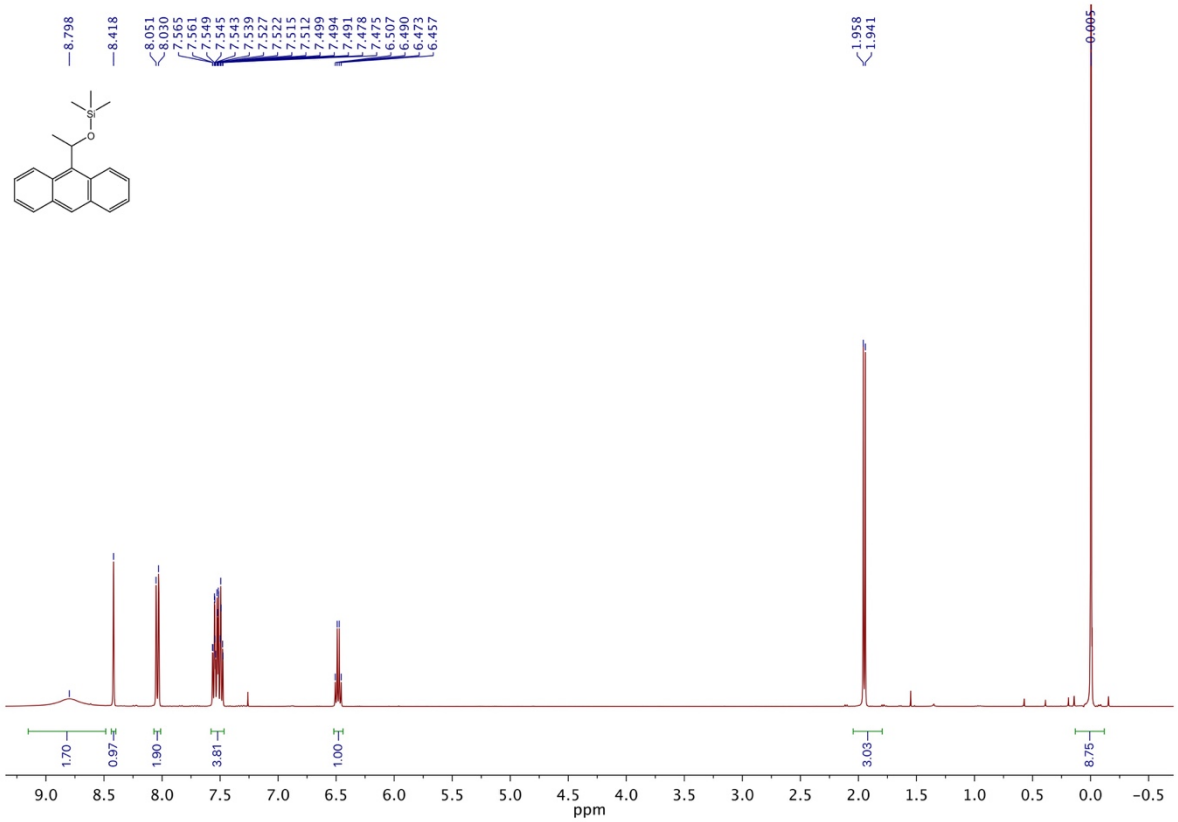


Figure S89: ^{1}H NMR spectrum of silyl ether **5da** (400 MHz, $CDCl_3$).

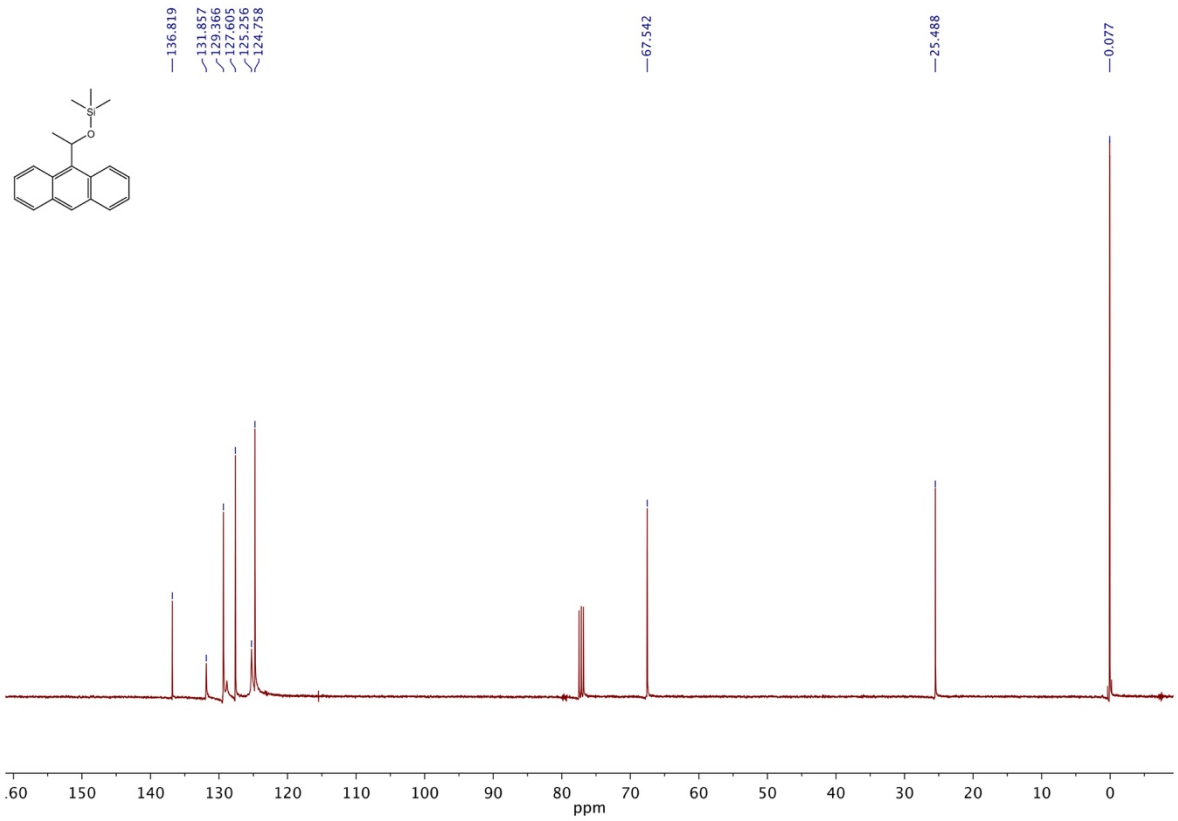


Figure S90: ^{13}C NMR spectrum of silyl ether **5da** (101 MHz, $CDCl_3$).

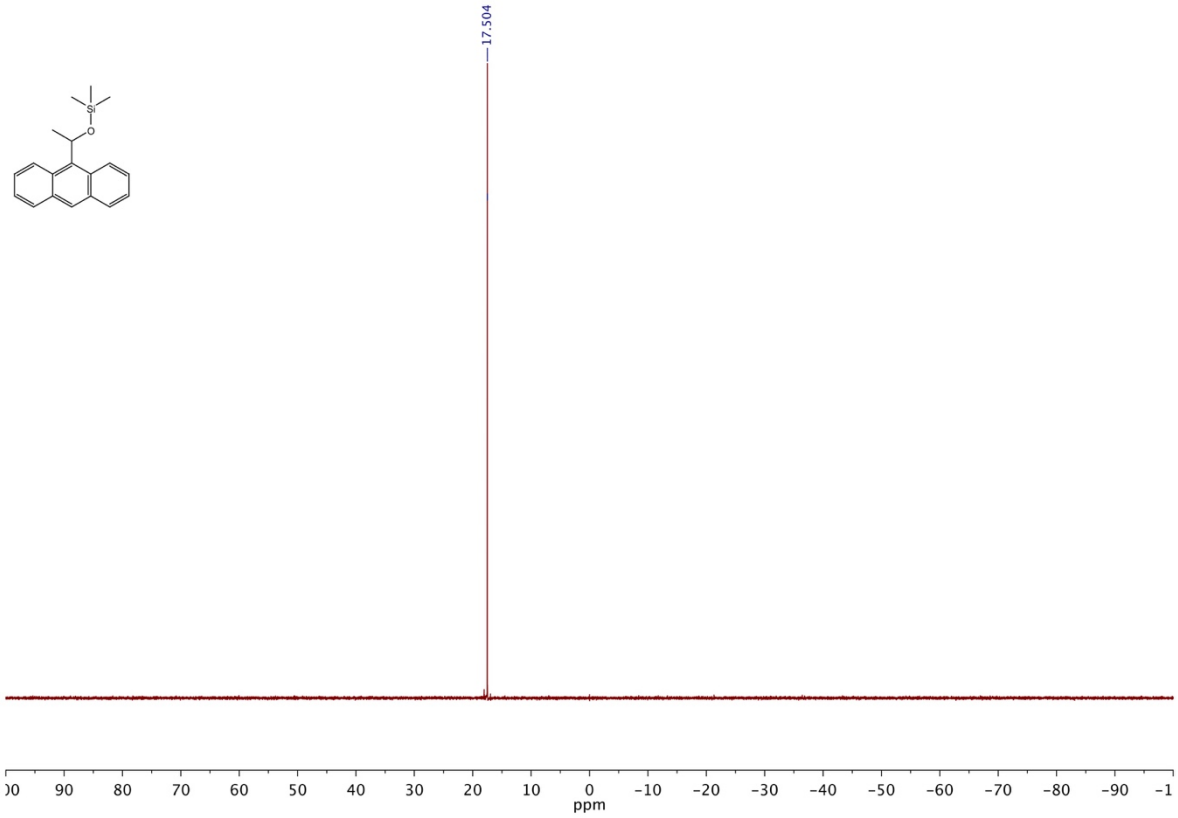


Figure S91: ^{29}Si NMR spectrum of silyl ether **5da** (79 MHz, $CDCl_3$).

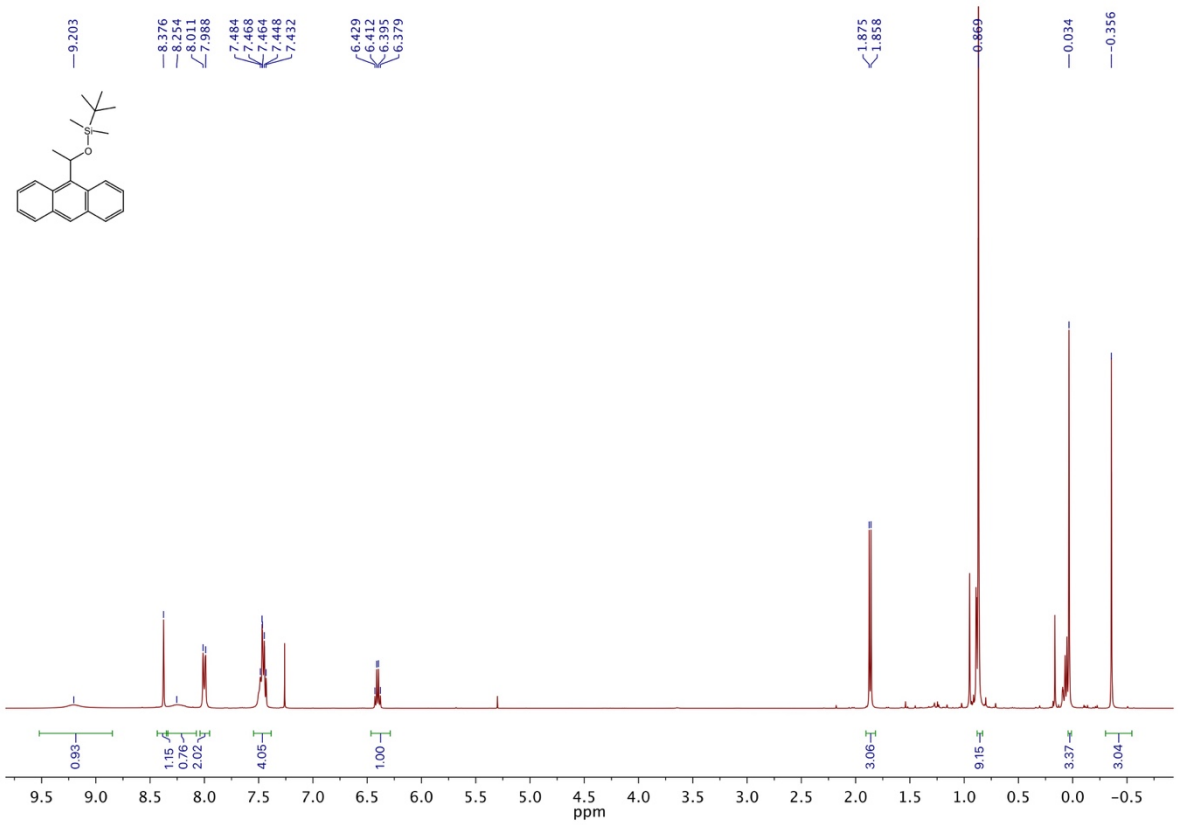


Figure S92: ^{1}H NMR spectrum of silyl ether **5db** (400 MHz, $CDCl_3$).

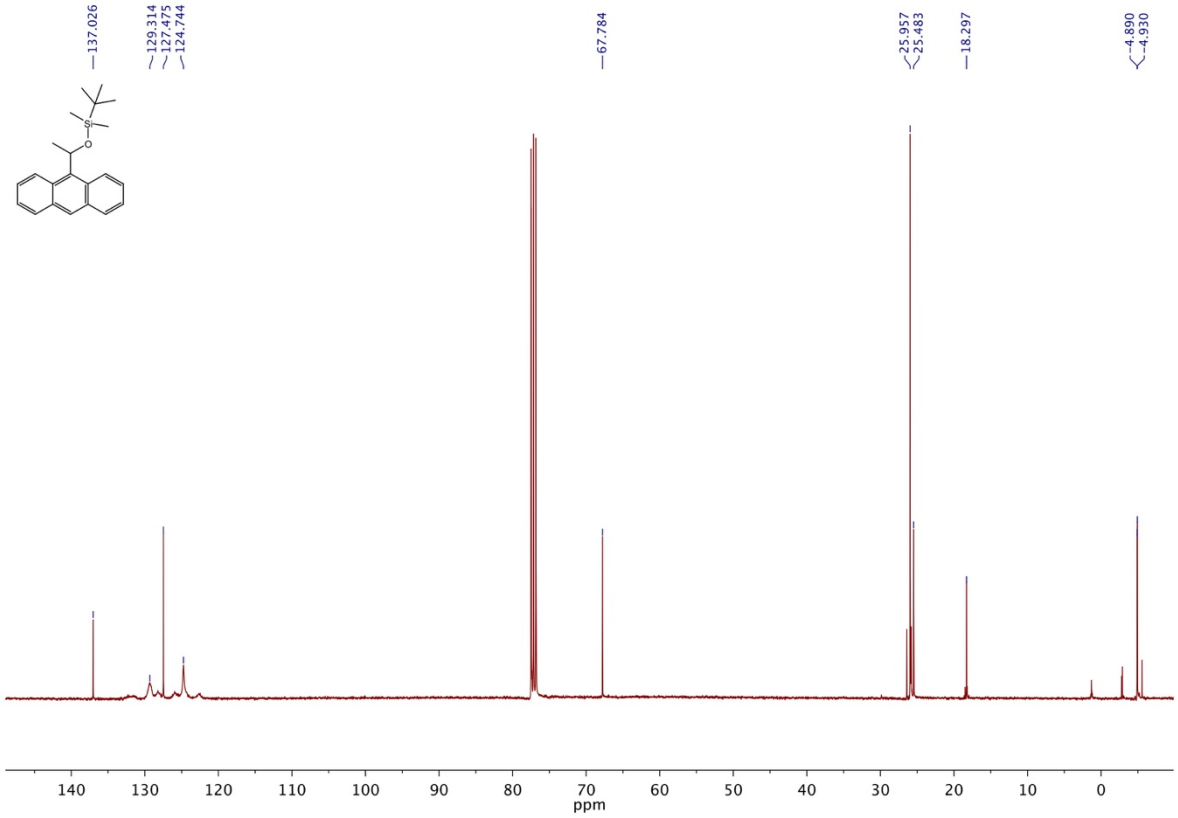


Figure S93: ^{13}C NMR spectrum of silyl ether **5db** (101 MHz, $CDCl_3$).

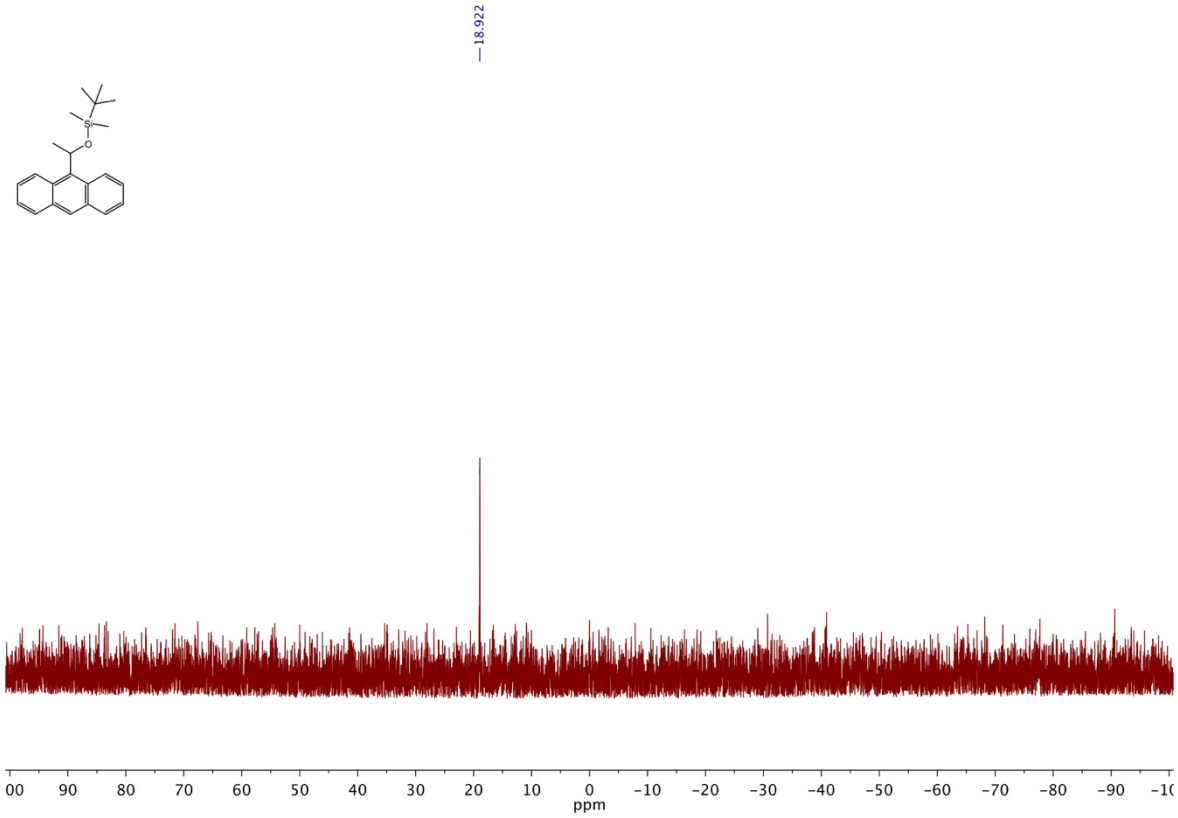


Figure S94: ^{29}Si NMR spectrum of silyl ether **5db** (79 MHz, $CDCl_3$).

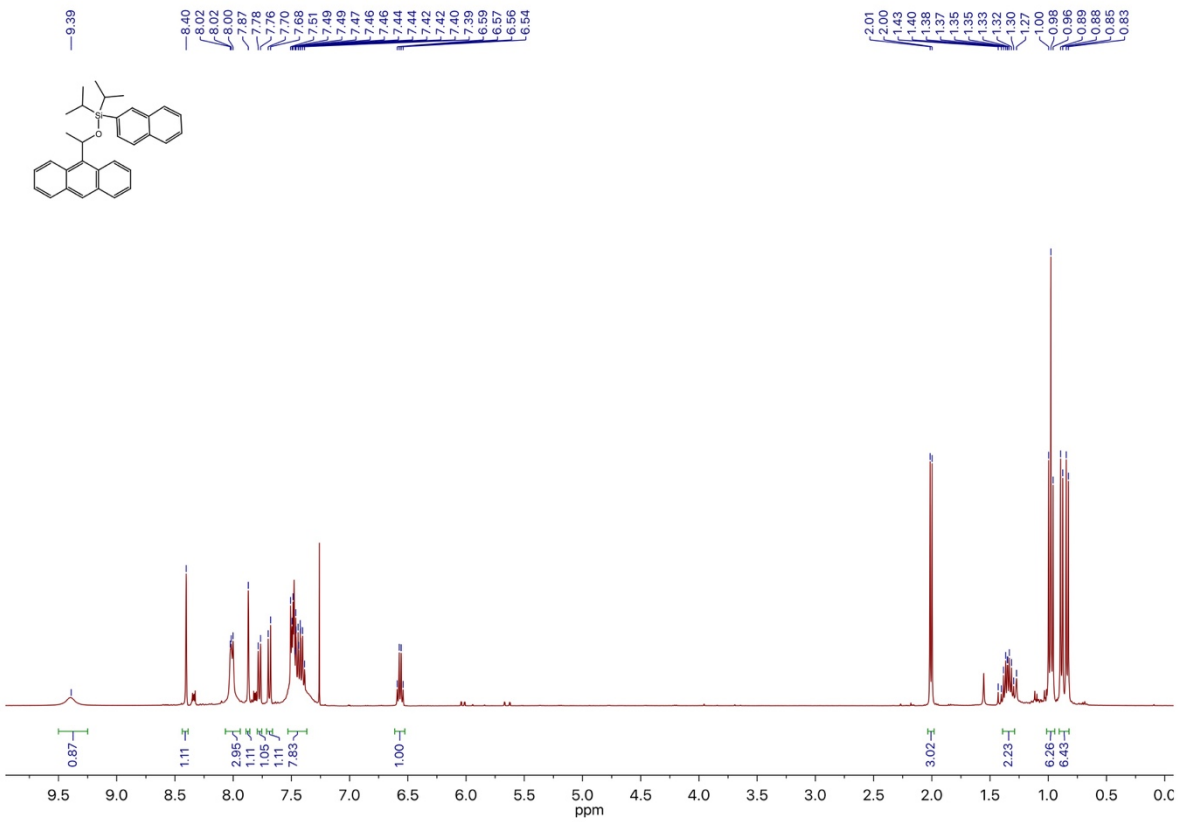


Figure S95: ^{1}H NMR spectrum of silyl ether **5dc** (400 MHz, $CDCl_3$).

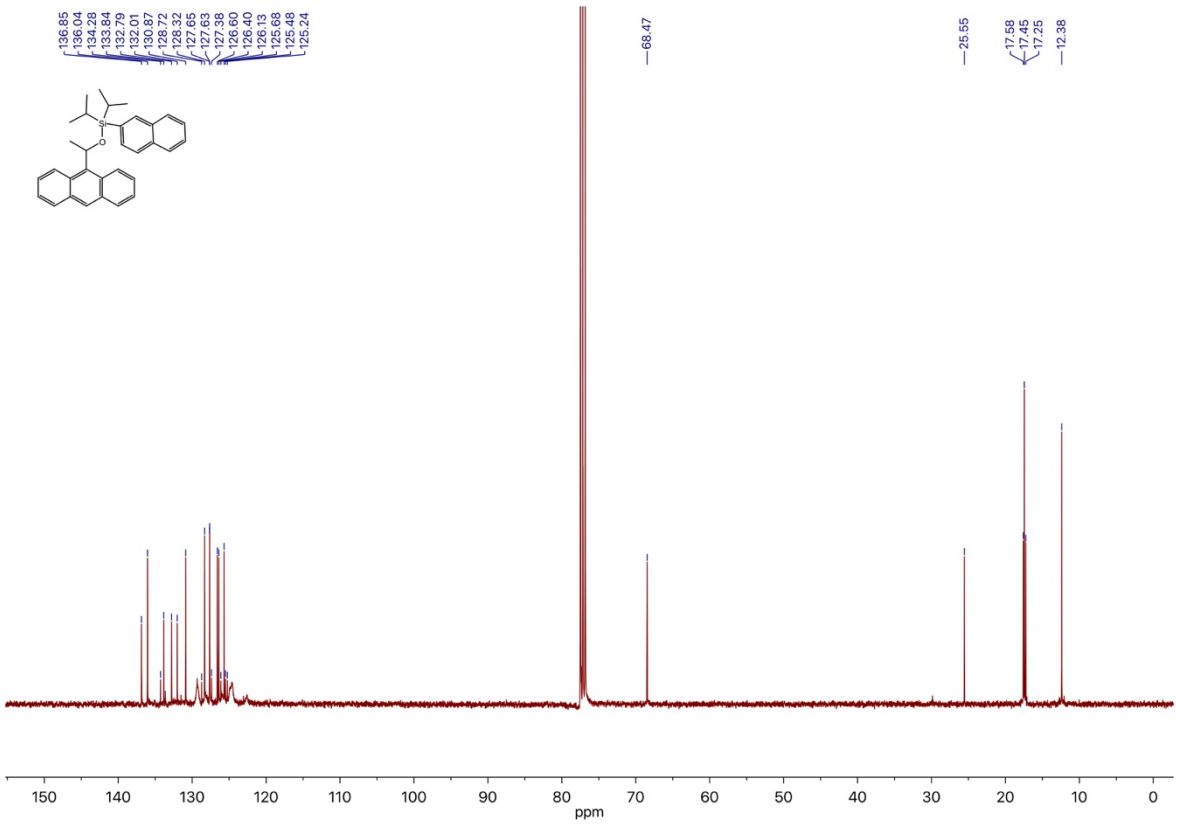


Figure S96: ^{13}C NMR spectrum of silyl ether **5dc** (101 MHz, $CDCl_3$).

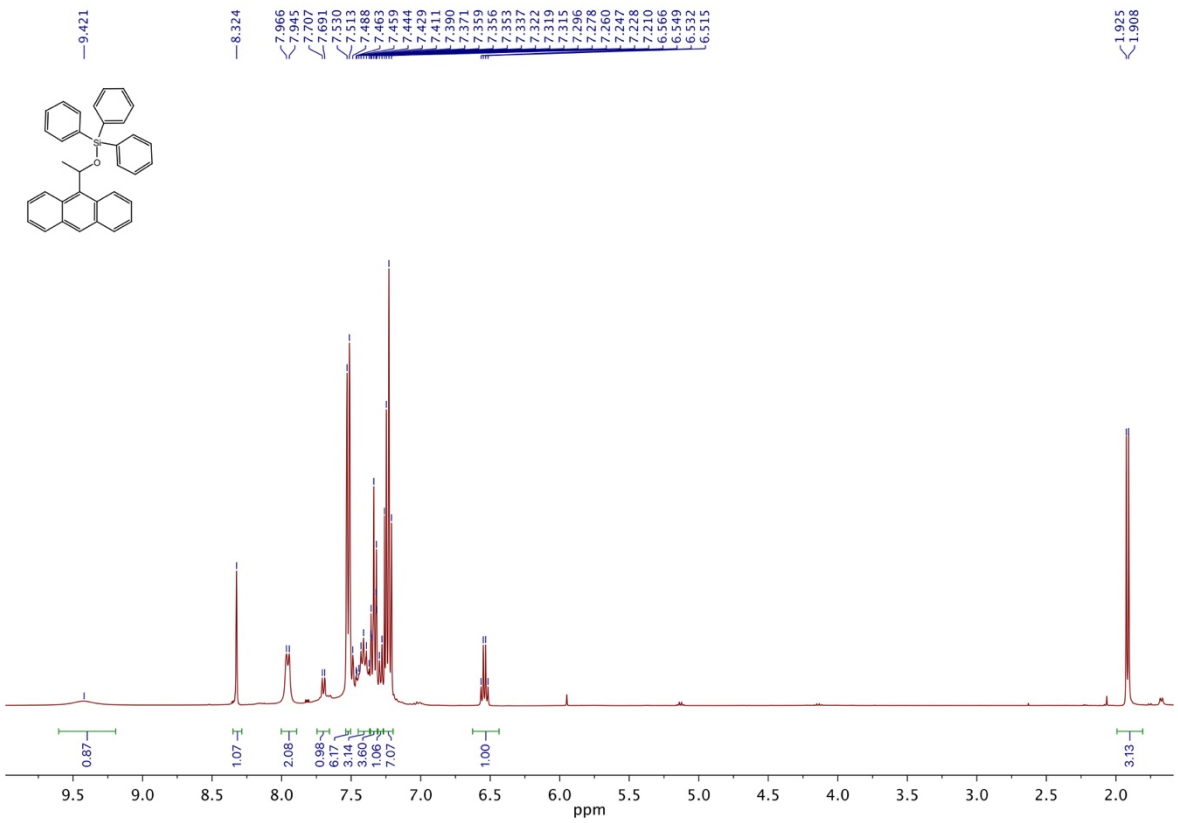


Figure S97: ^{1}H NMR spectrum of silyl ether **5dd** (400 MHz, $CDCl_3$).

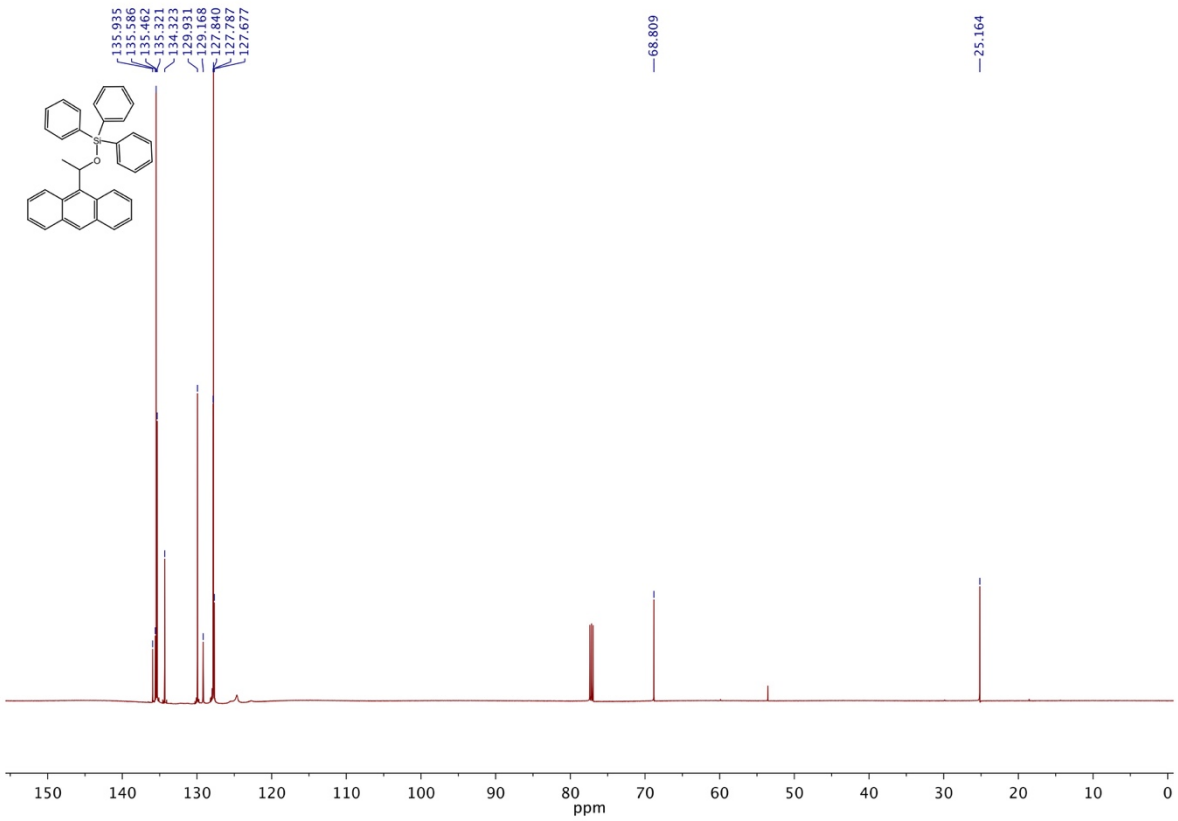


Figure S98: ^{13}C NMR spectrum of silyl ether **5dd** (101 MHz, $CDCl_3$).

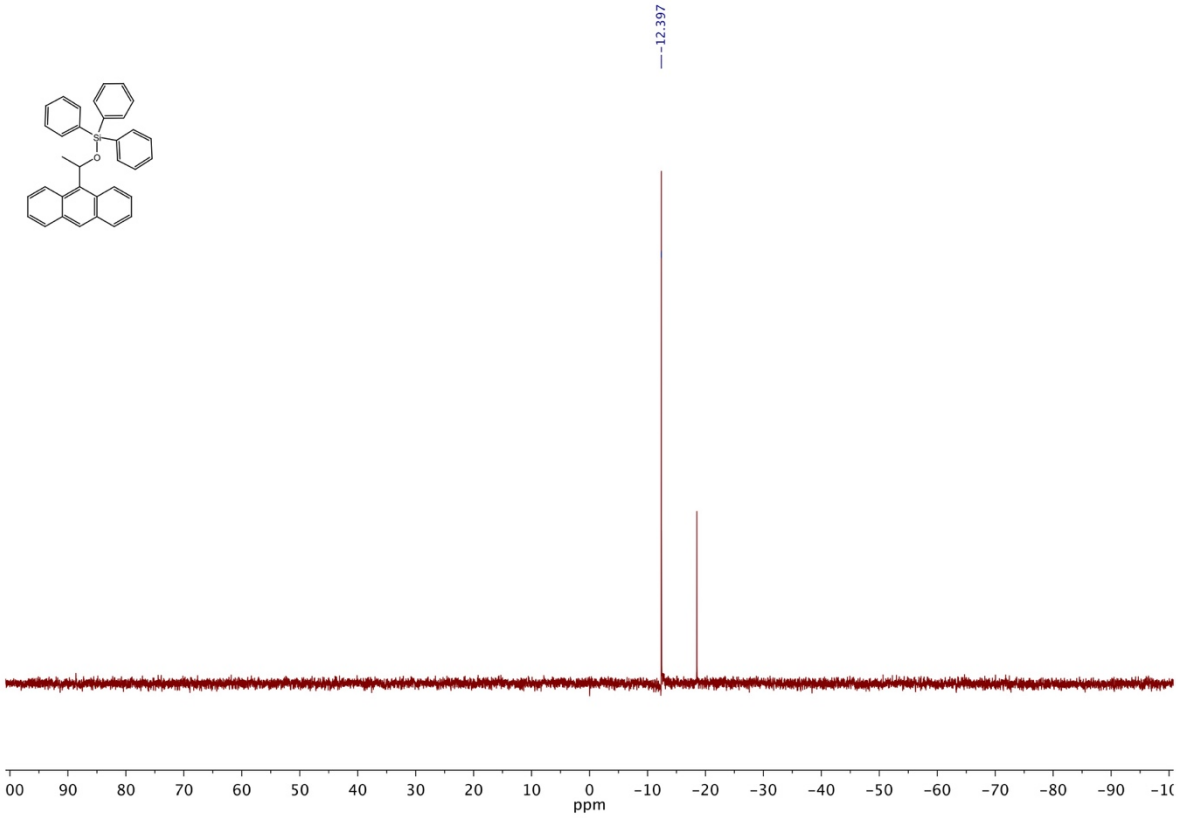


Figure S99: ^{29}Si NMR spectrum of silyl ether **5dd** (79 MHz, $CDCl_3$).

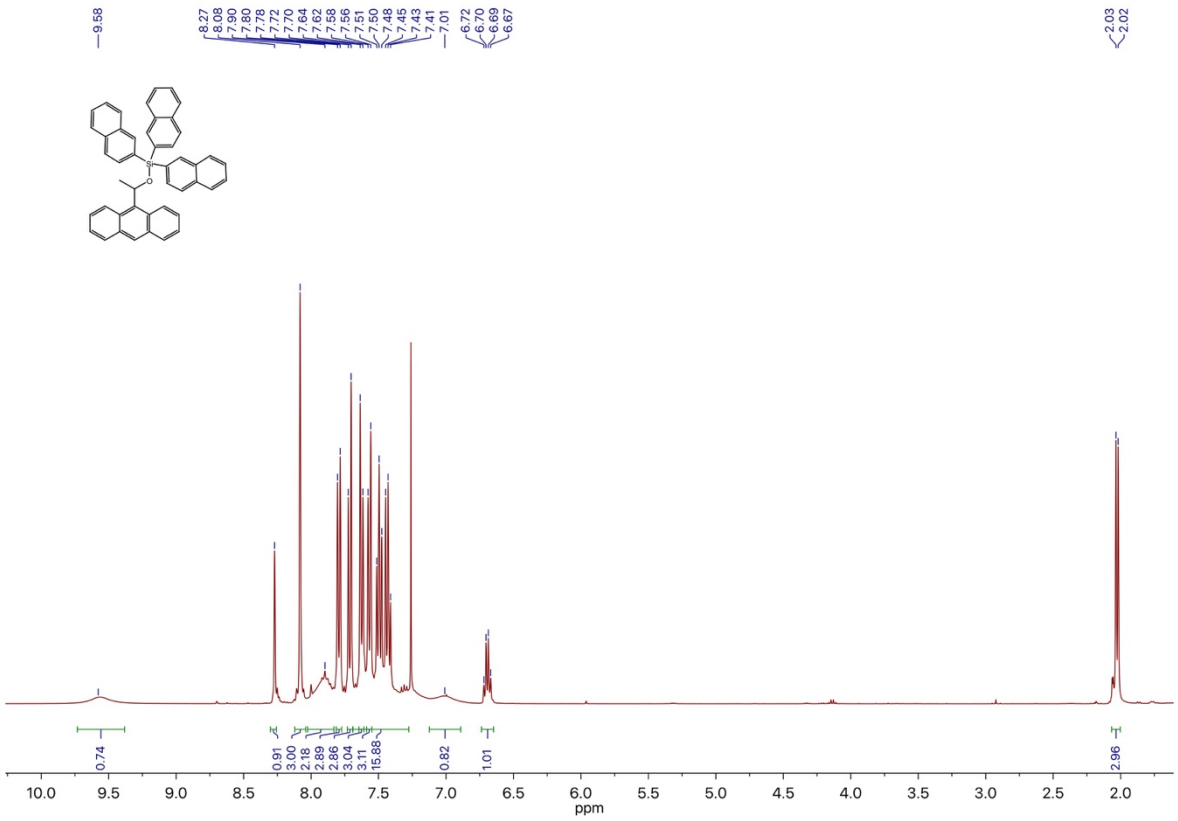


Figure S100: ^{1}H NMR spectrum of silyl ether **5de** (400 MHz, $CDCl_3$).

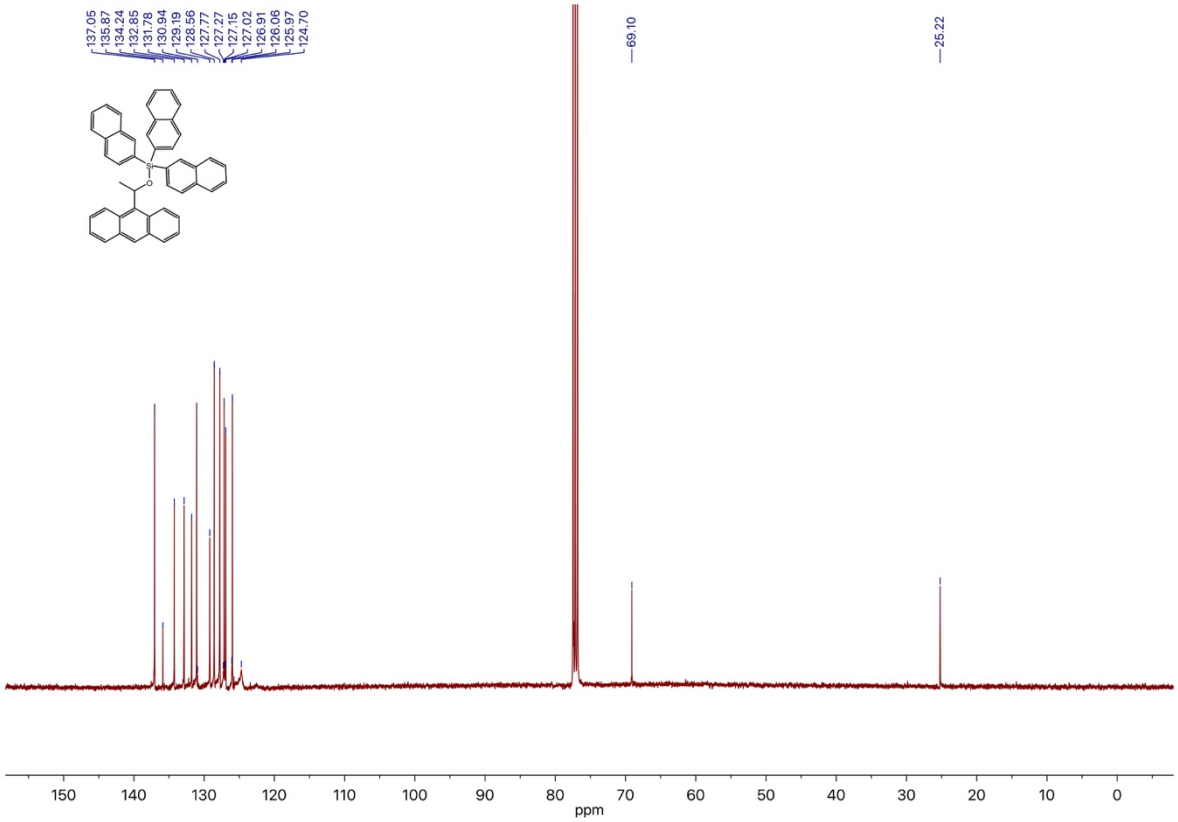


Figure S101: ^{13}C NMR spectrum of silyl ether **5de** (101 MHz, $CDCl_3$).

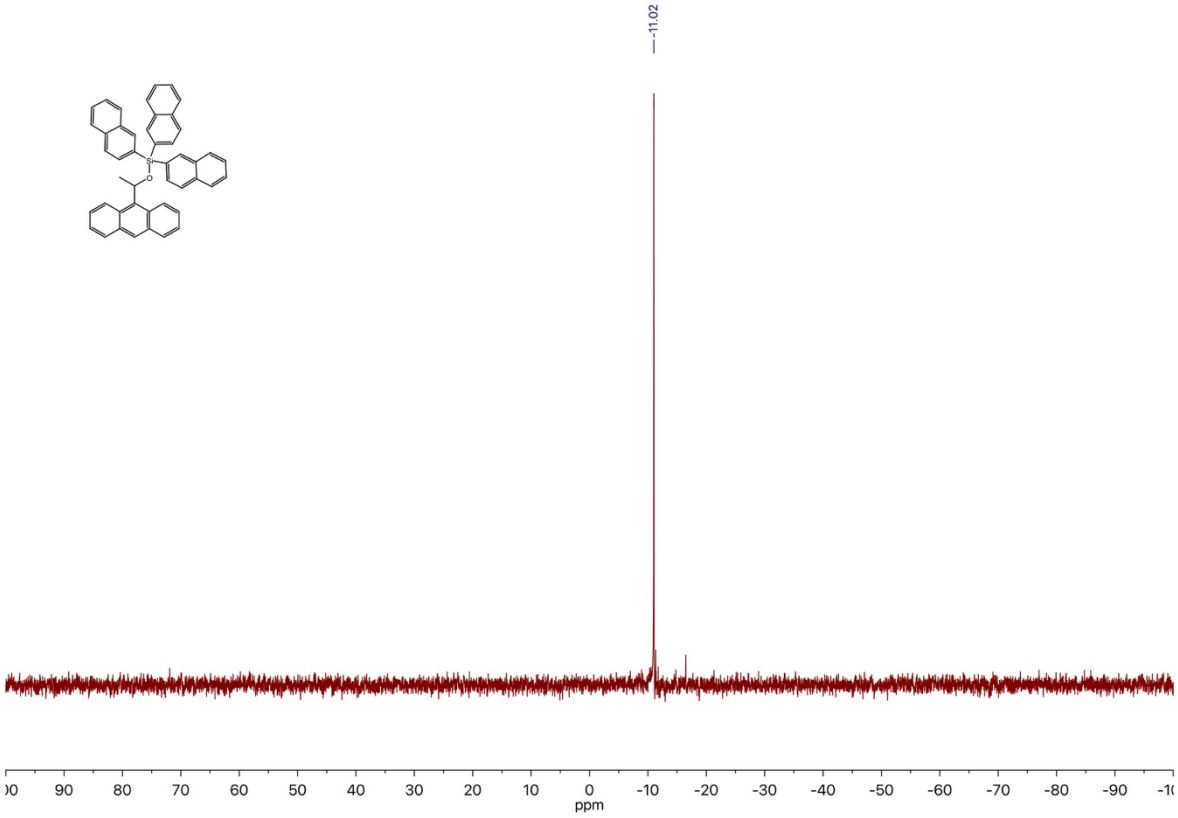


Figure S102: ^{29}Si NMR spectrum of silyl ether **5de** (79 MHz, $CDCl_3$).

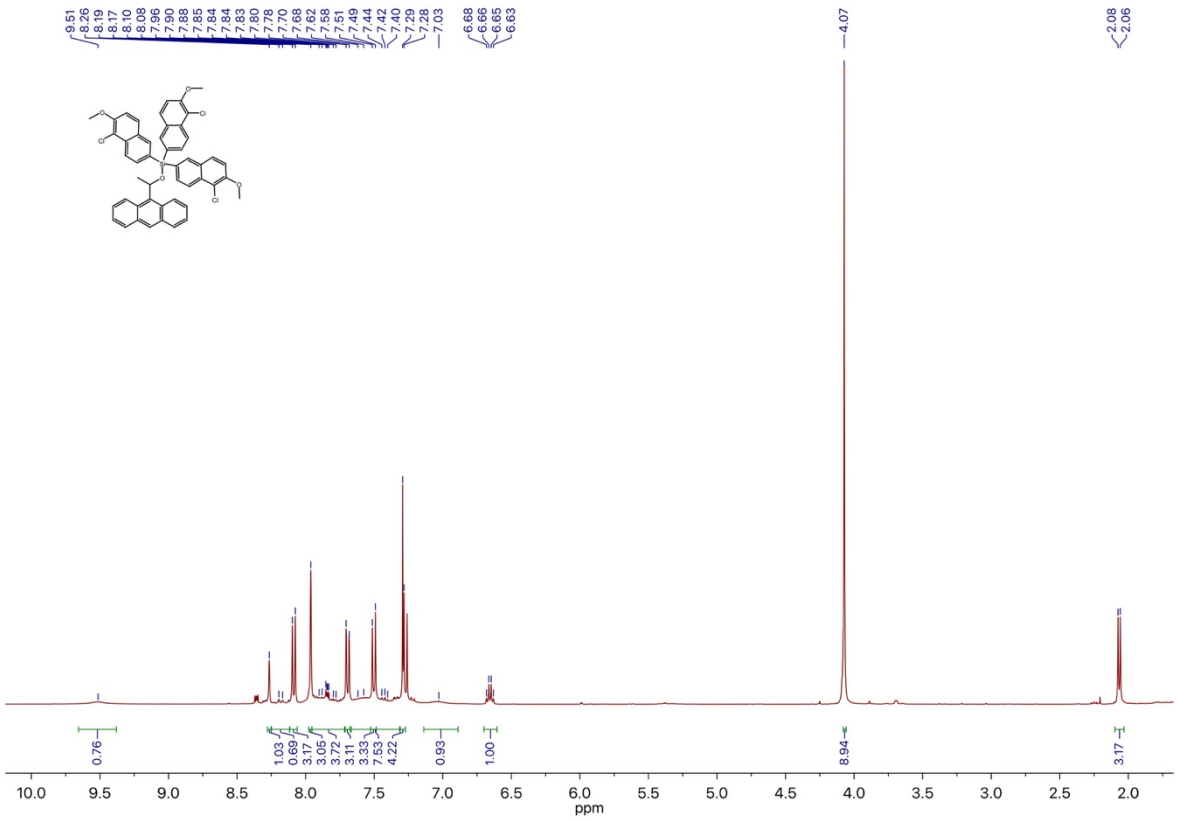


Figure S103: ^{1}H NMR spectrum of silyl ether **5df** (400 MHz, $CDCl_3$).

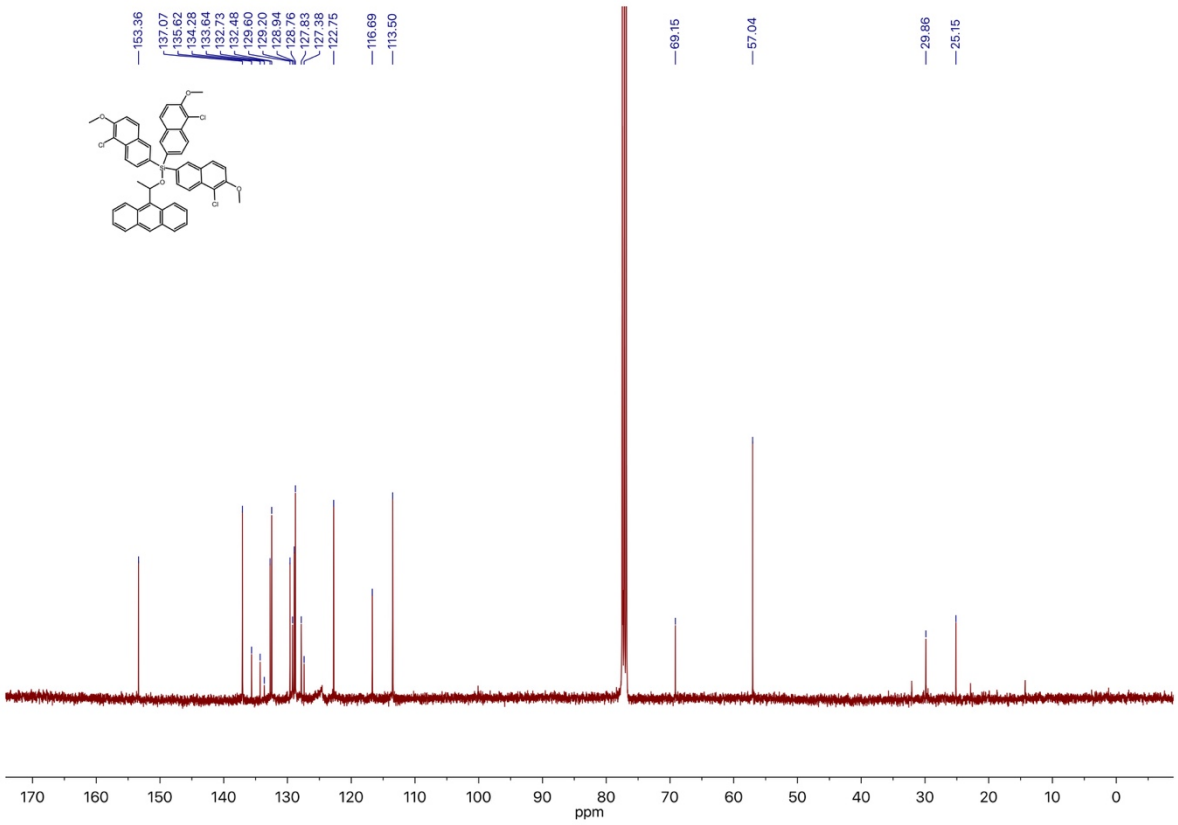


Figure S104: ^{13}C NMR spectrum of silyl ether **5df** (101 MHz, $CDCl_3$).

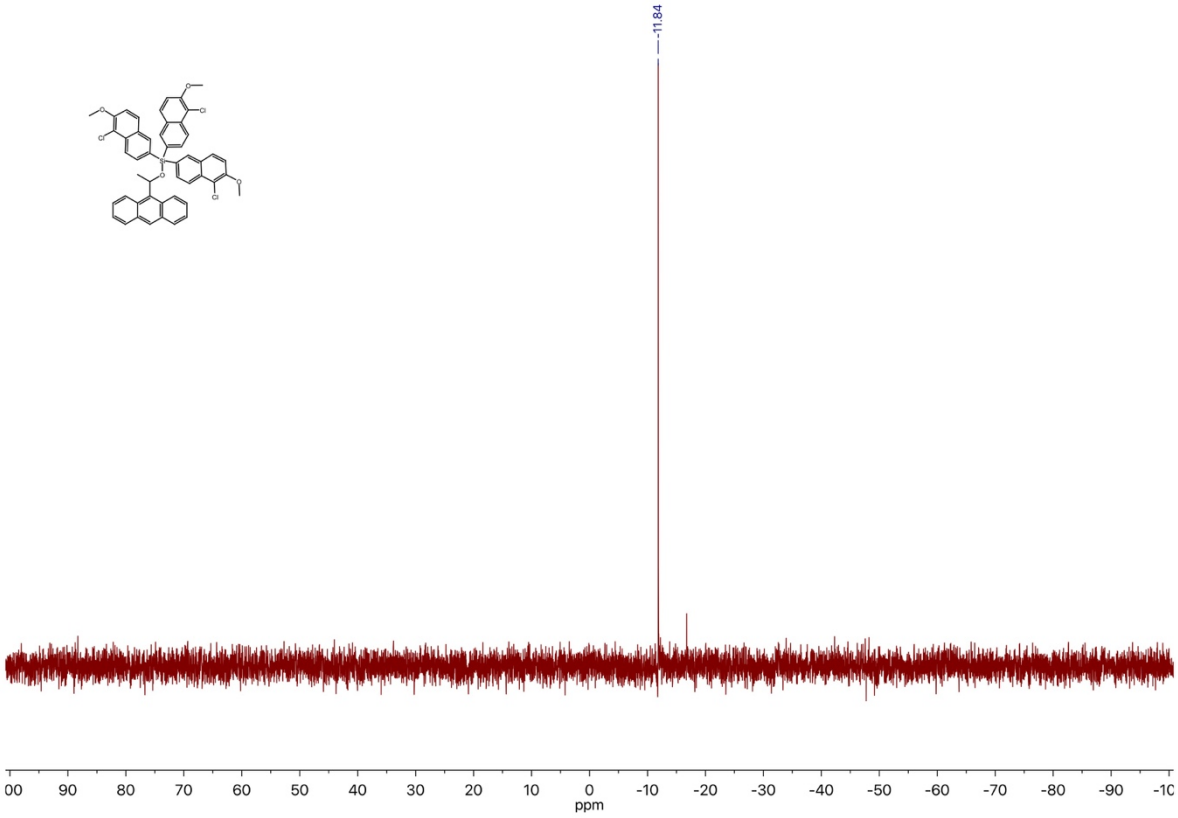


Figure S105: ^{29}Si NMR spectrum of silyl ether **5df** (79 MHz, $CDCl_3$).

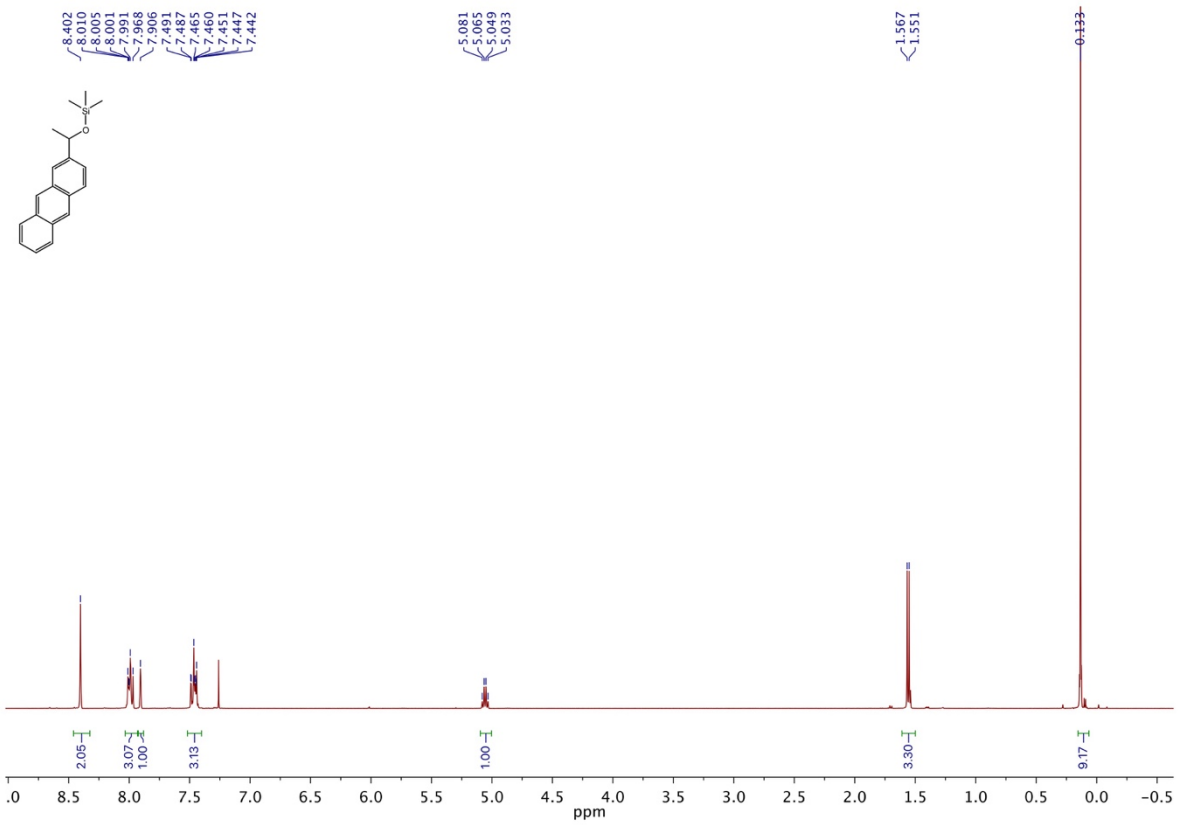


Figure S106: ^{1}H NMR spectrum of silyl ether **5ea** (400 MHz, $CDCl_3$).

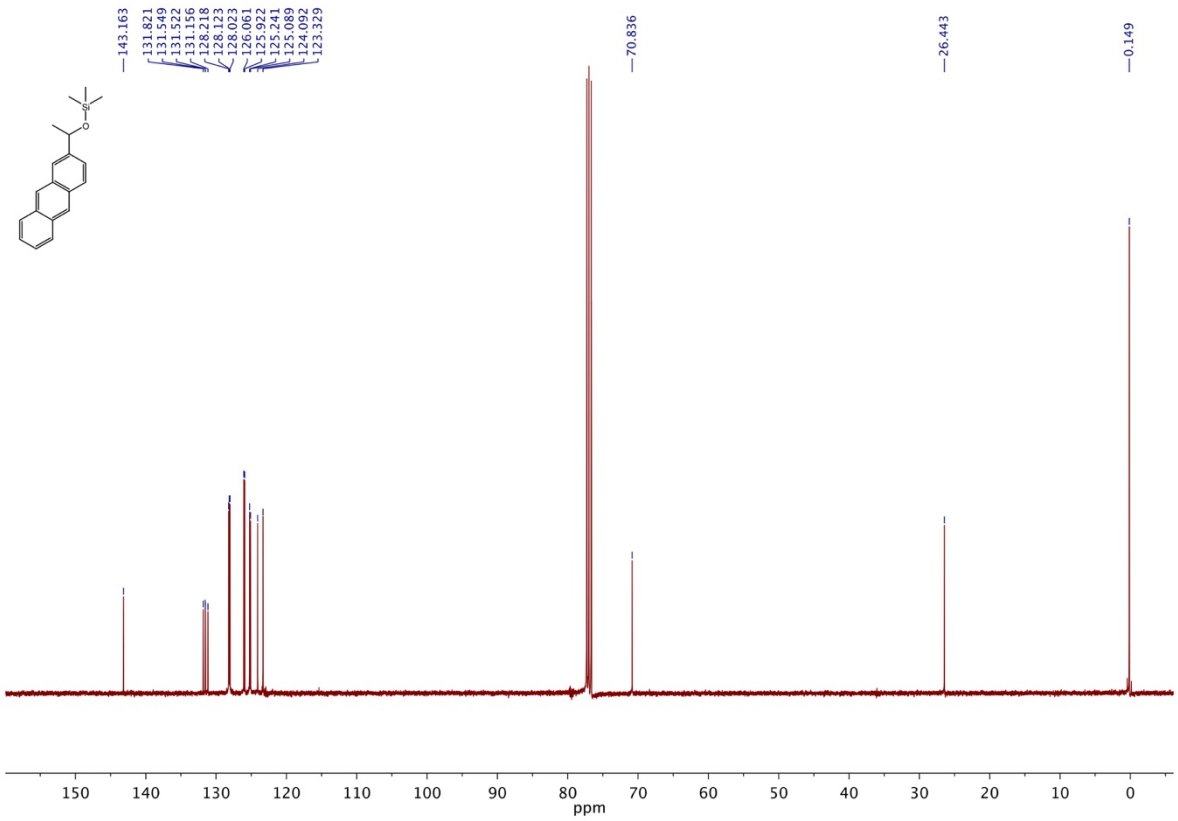


Figure S107: ^{13}C NMR spectrum of silyl ether **5ea** (101 MHz, $CDCl_3$).

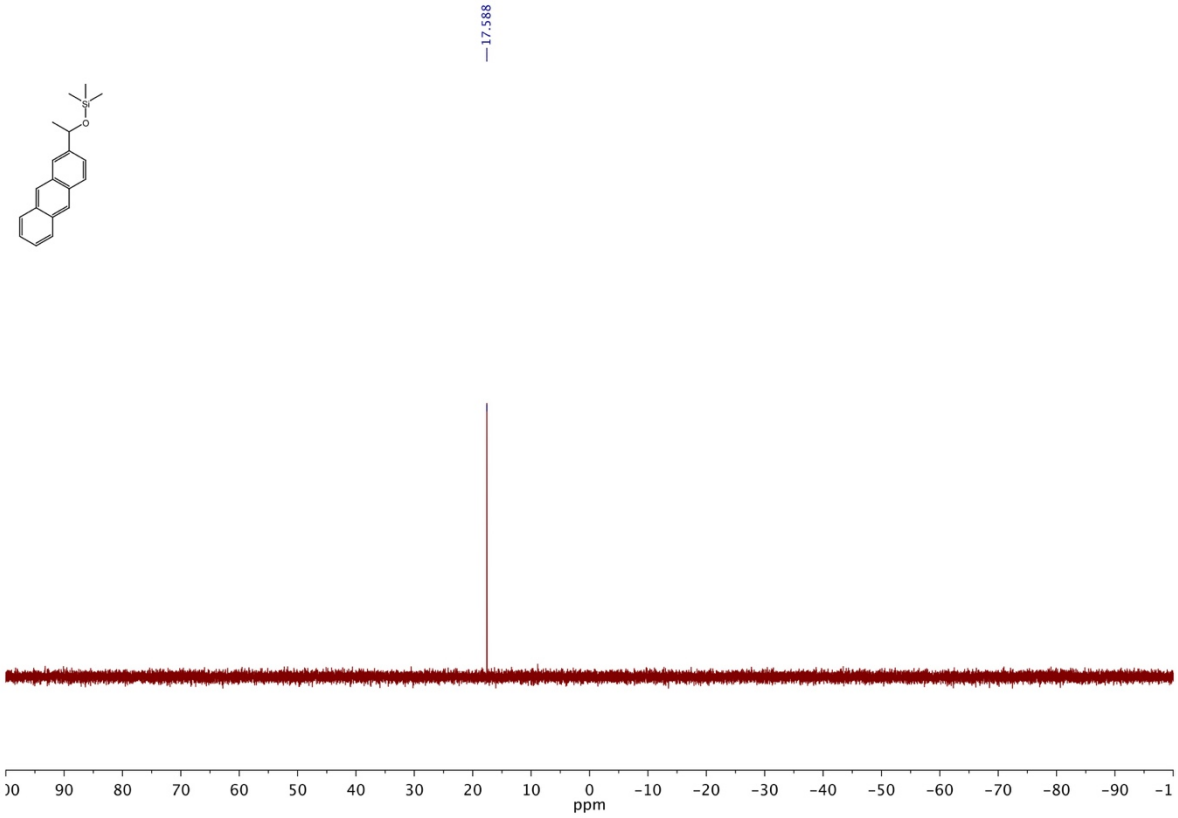


Figure S108: ^{29}Si NMR spectrum of silyl ether **5ea** (79 MHz, $CDCl_3$).

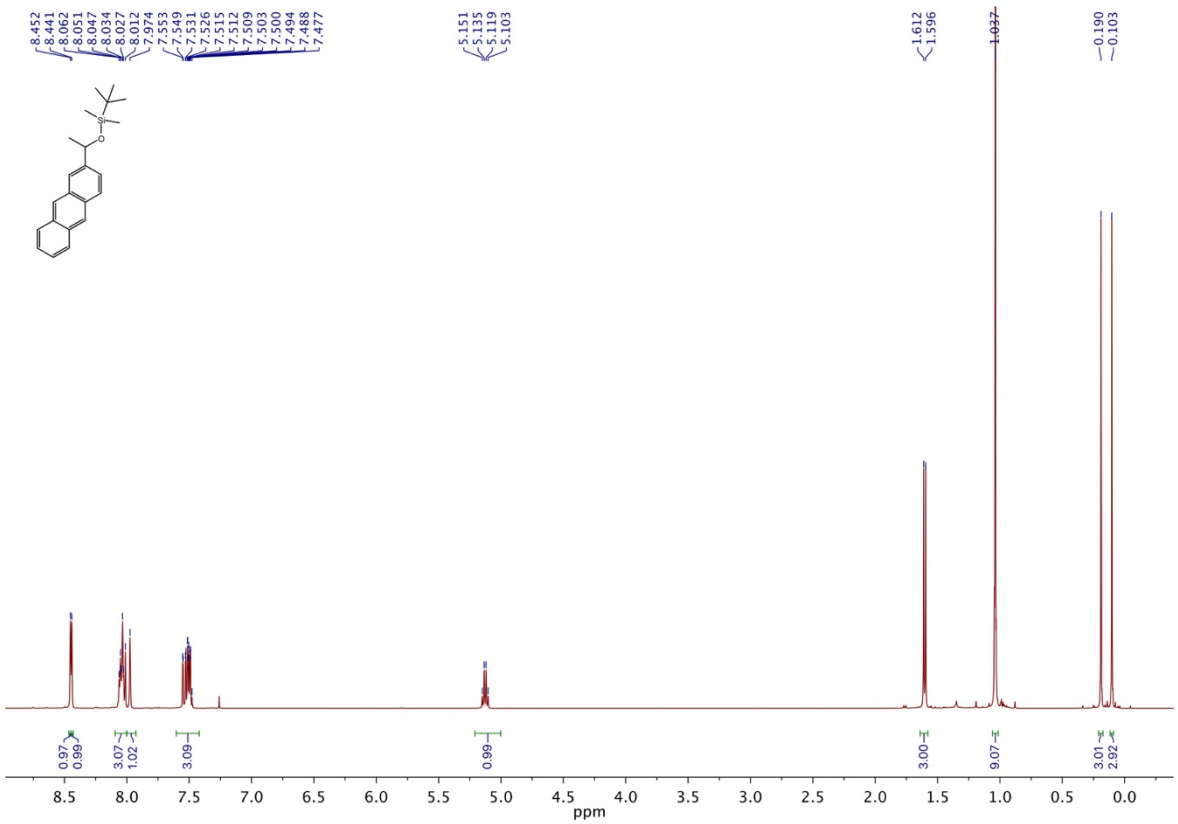


Figure S109: ^{1}H NMR spectrum of silyl ether **5eb** (400 MHz, $CDCl_3$).

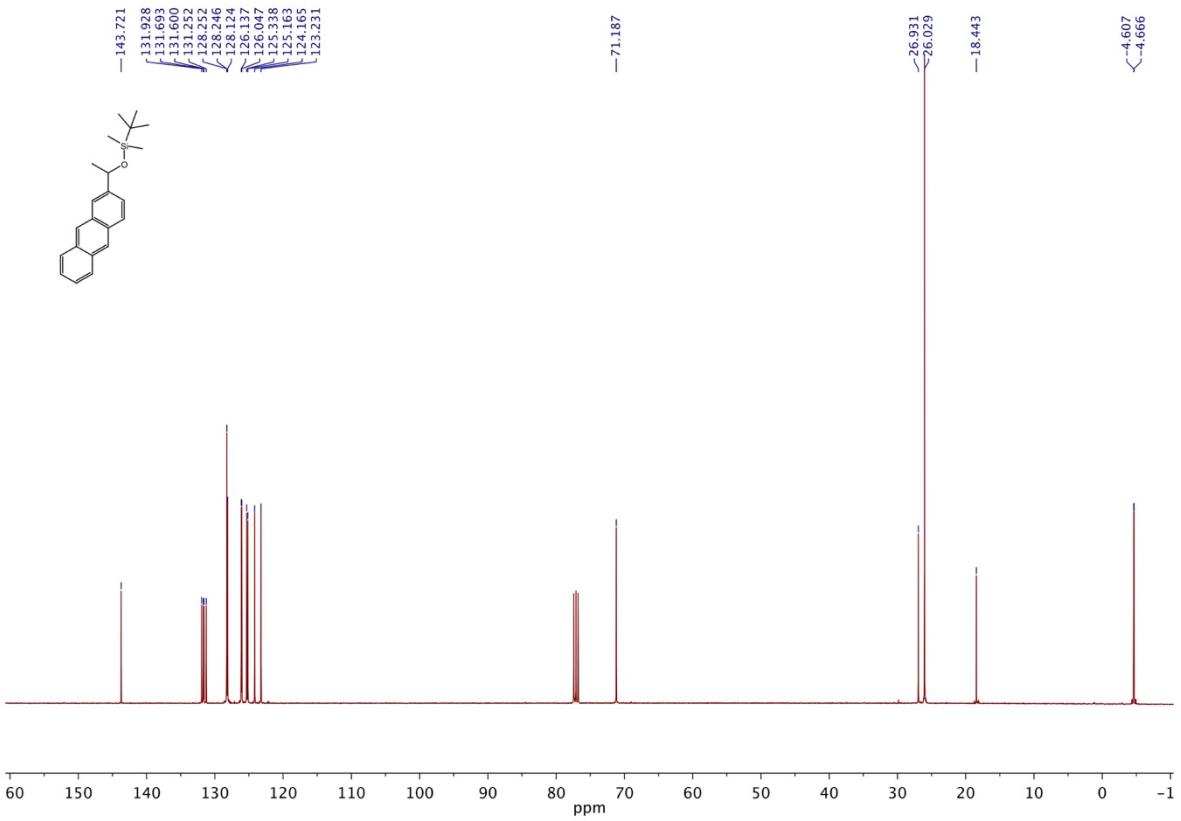


Figure S110: ^{13}C NMR spectrum of silyl ether **5eb** (101 MHz, $CDCl_3$).

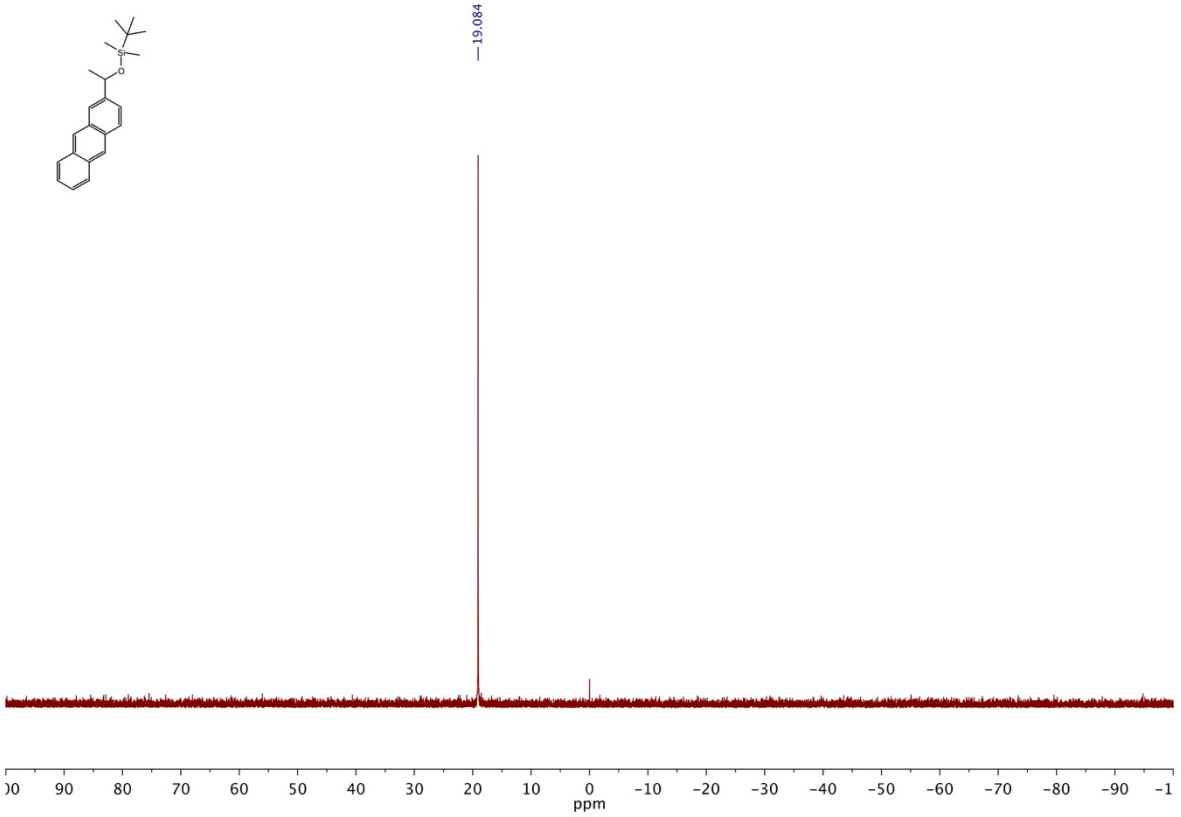


Figure S111: ^{29}Si NMR spectrum of silyl ether **5eb** (79 MHz, $CDCl_3$).

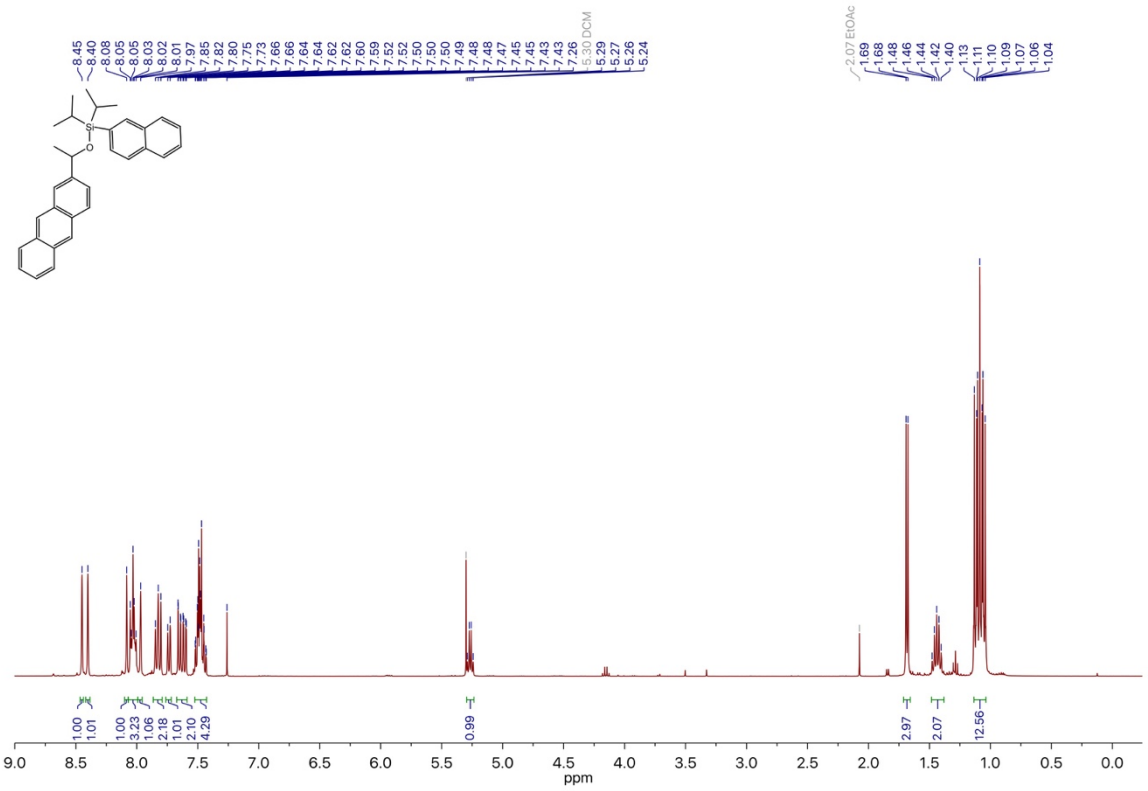


Figure S112: ^{1}H NMR spectrum of silyl ether **5ec** (400 MHz, $CDCl_3$).

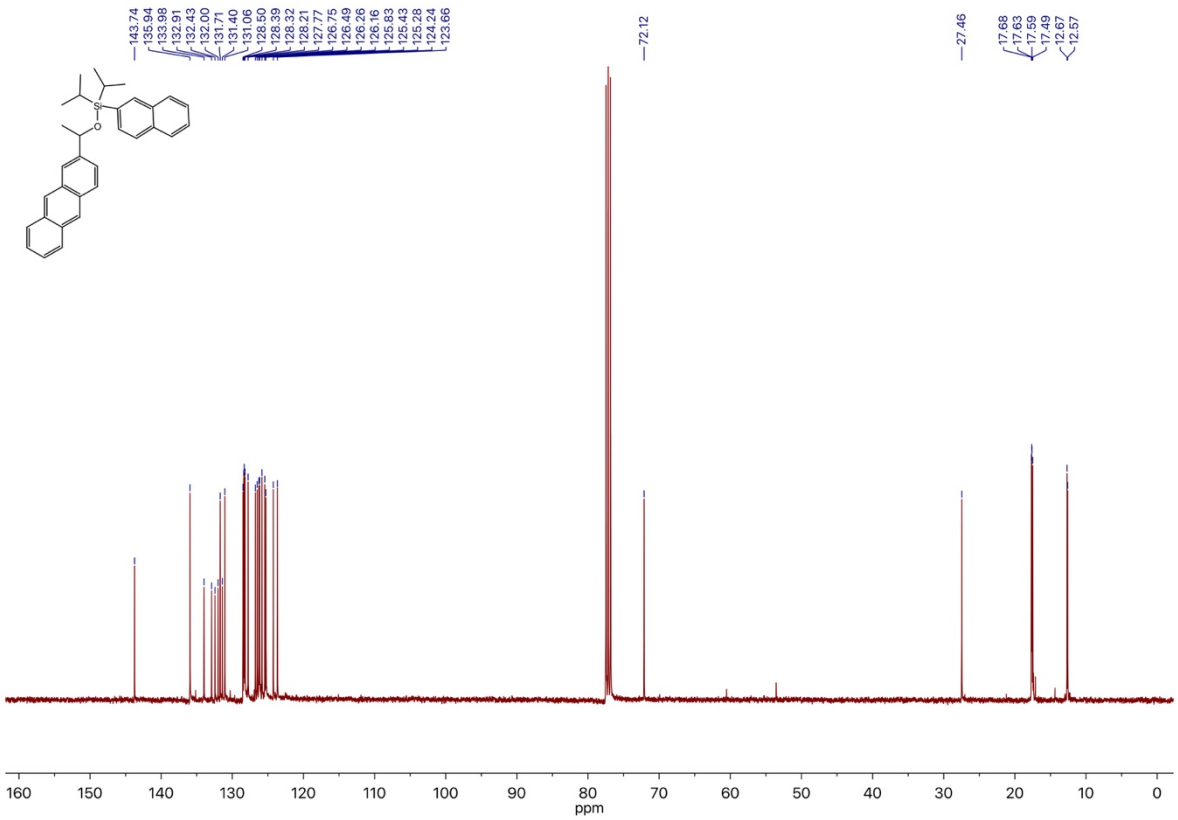


Figure S113: ^{13}C NMR spectrum of silyl ether **5ec** (101 MHz, $CDCl_3$).

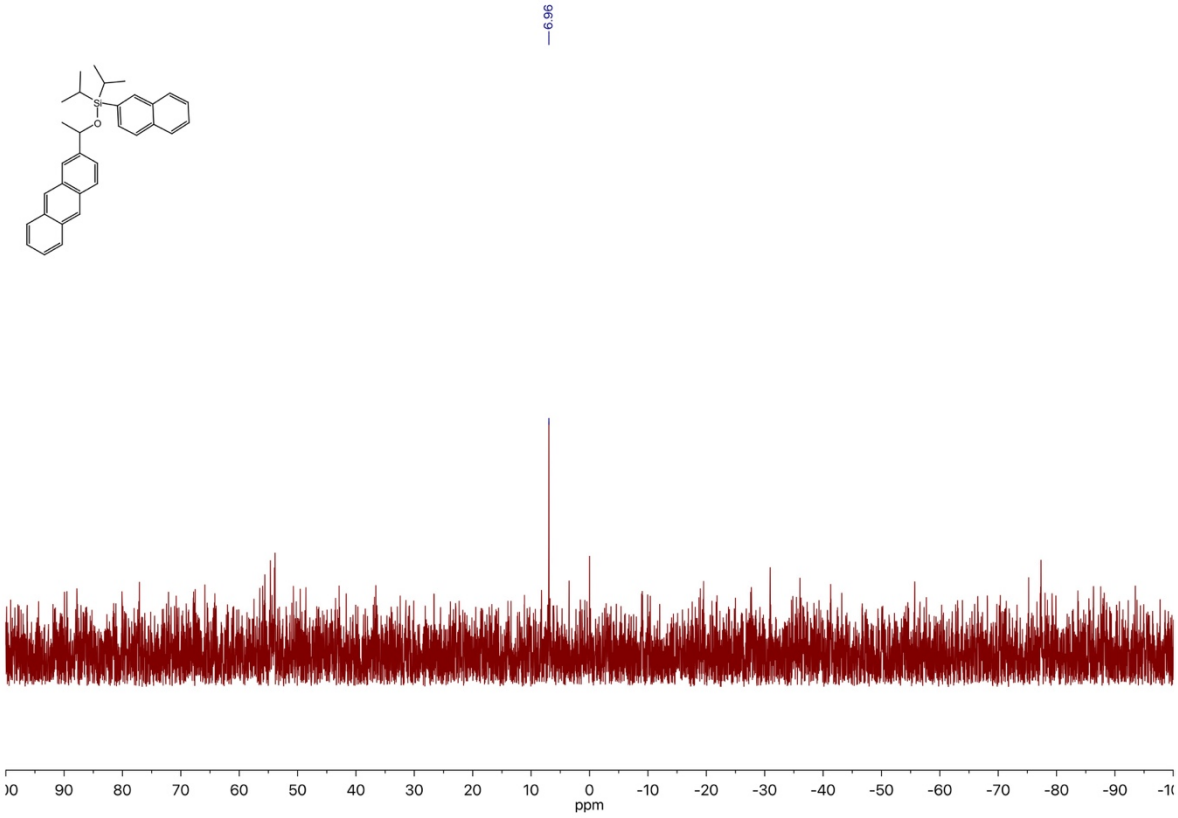


Figure S114: ^{29}Si NMR spectrum of silyl ether **5ec** (79 MHz, $CDCl_3$).

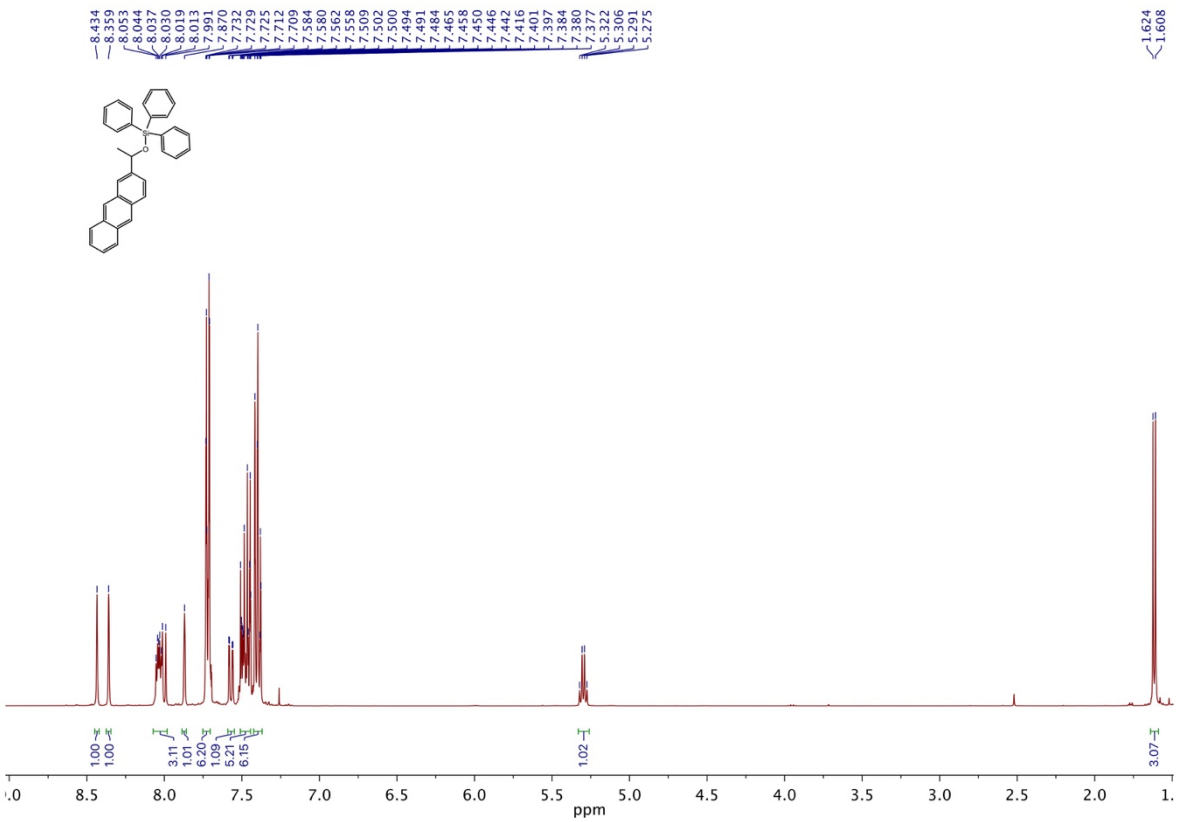


Figure S115: ^{1}H NMR spectrum of silyl ether **5ed** (400 MHz, $CDCl_3$).

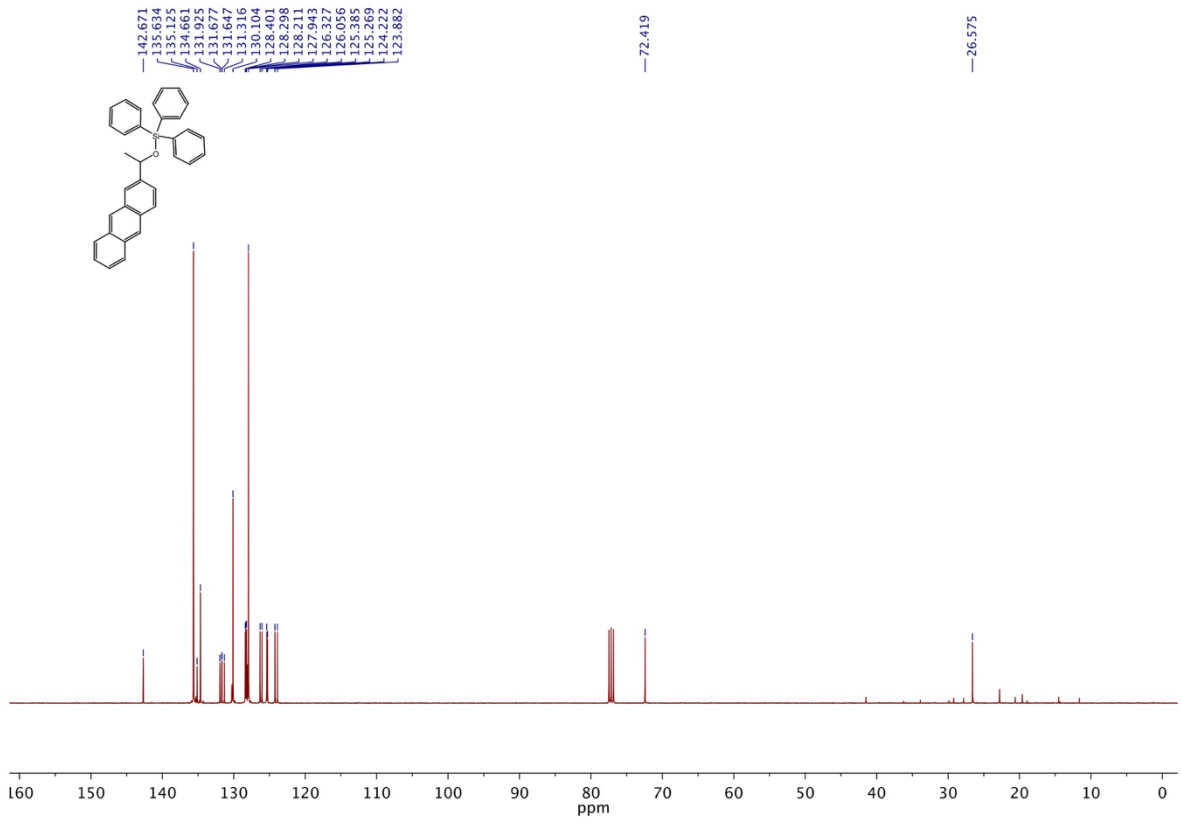


Figure S116: ^{13}C NMR spectrum of silyl ether **5ed** (101 MHz, $CDCl_3$).

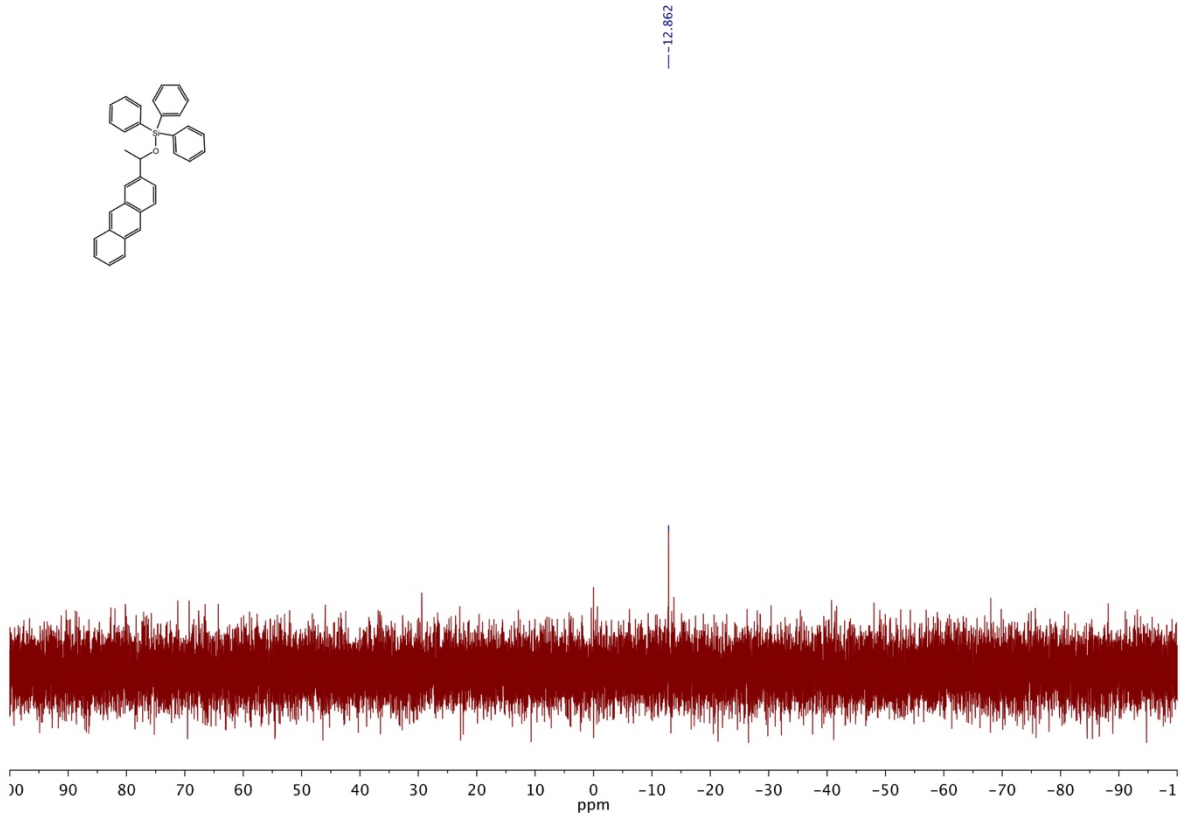


Figure S117: ^{29}Si NMR spectrum of silyl ether **5ed** (79 MHz, $CDCl_3$).

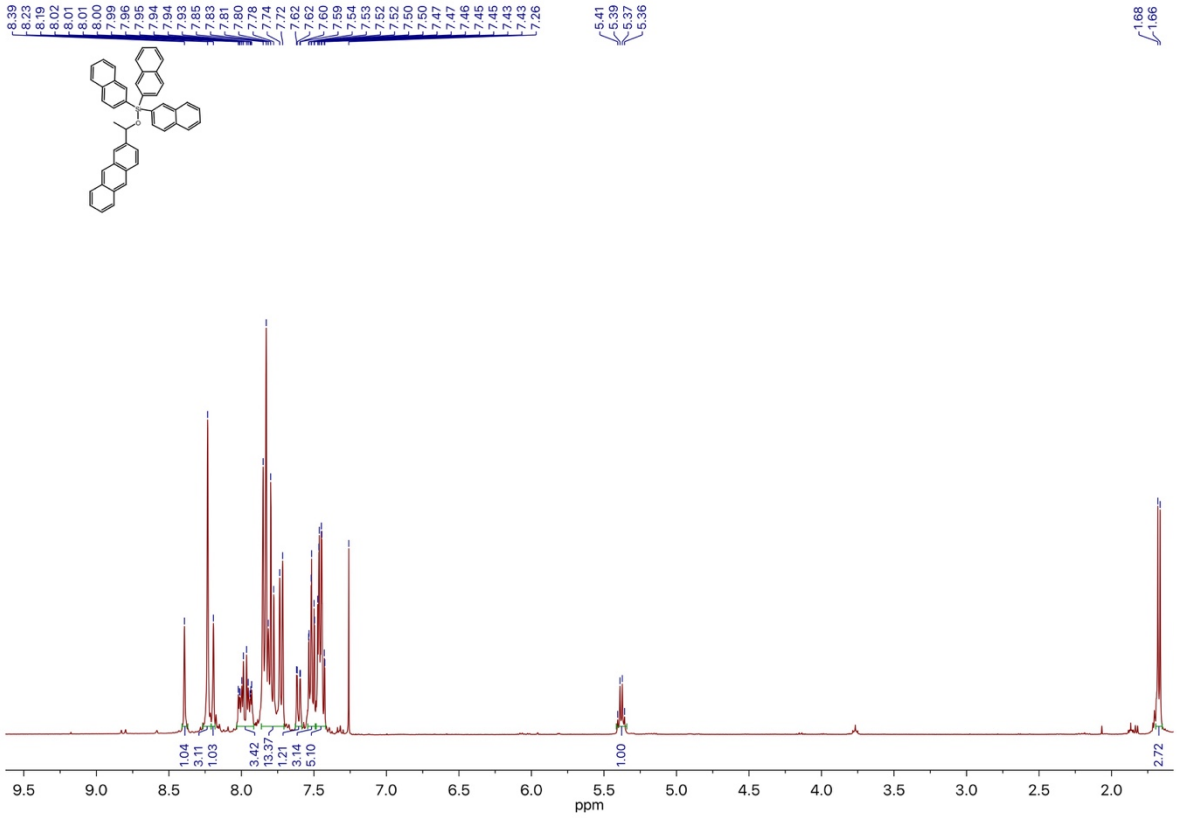


Figure S118: ^{1}H NMR spectrum of silyl ether **5ee** (400 MHz, $CDCl_3$).

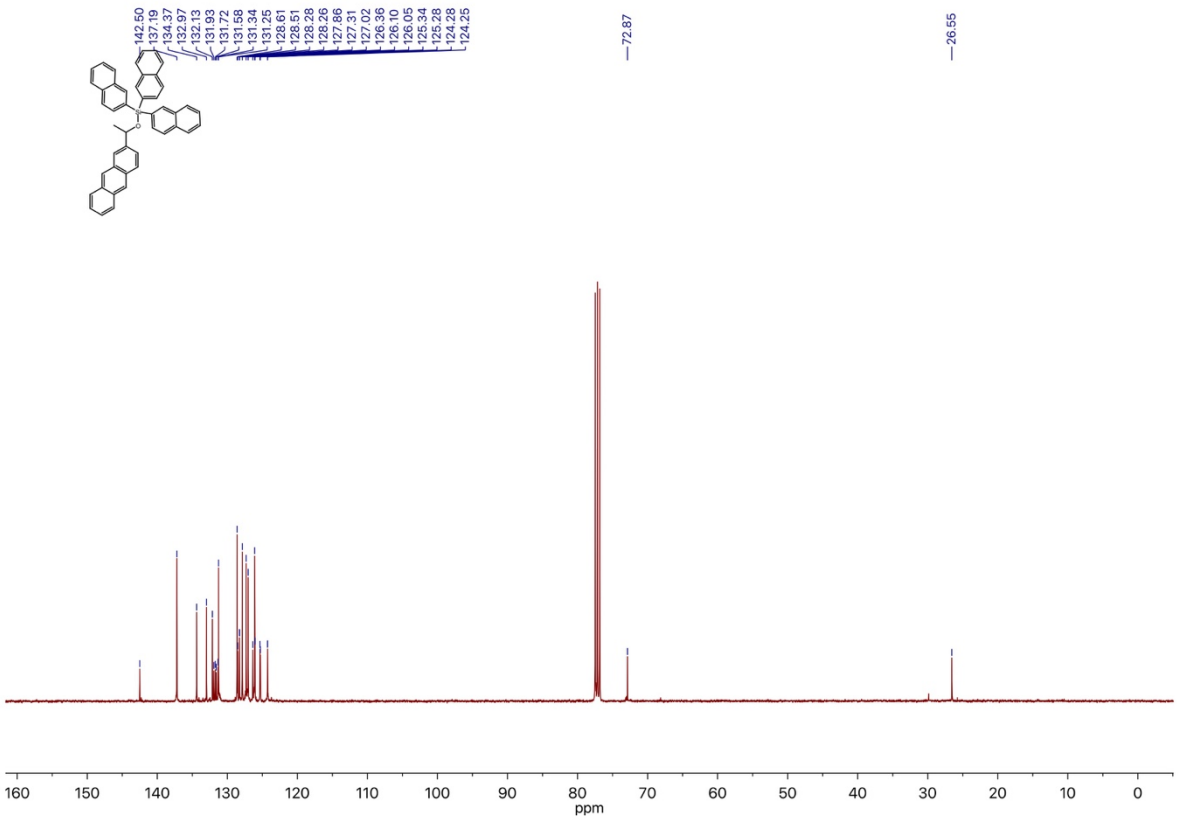


Figure S119: ^{13}C NMR spectrum of silyl ether **5ee** (101 MHz, $CDCl_3$).

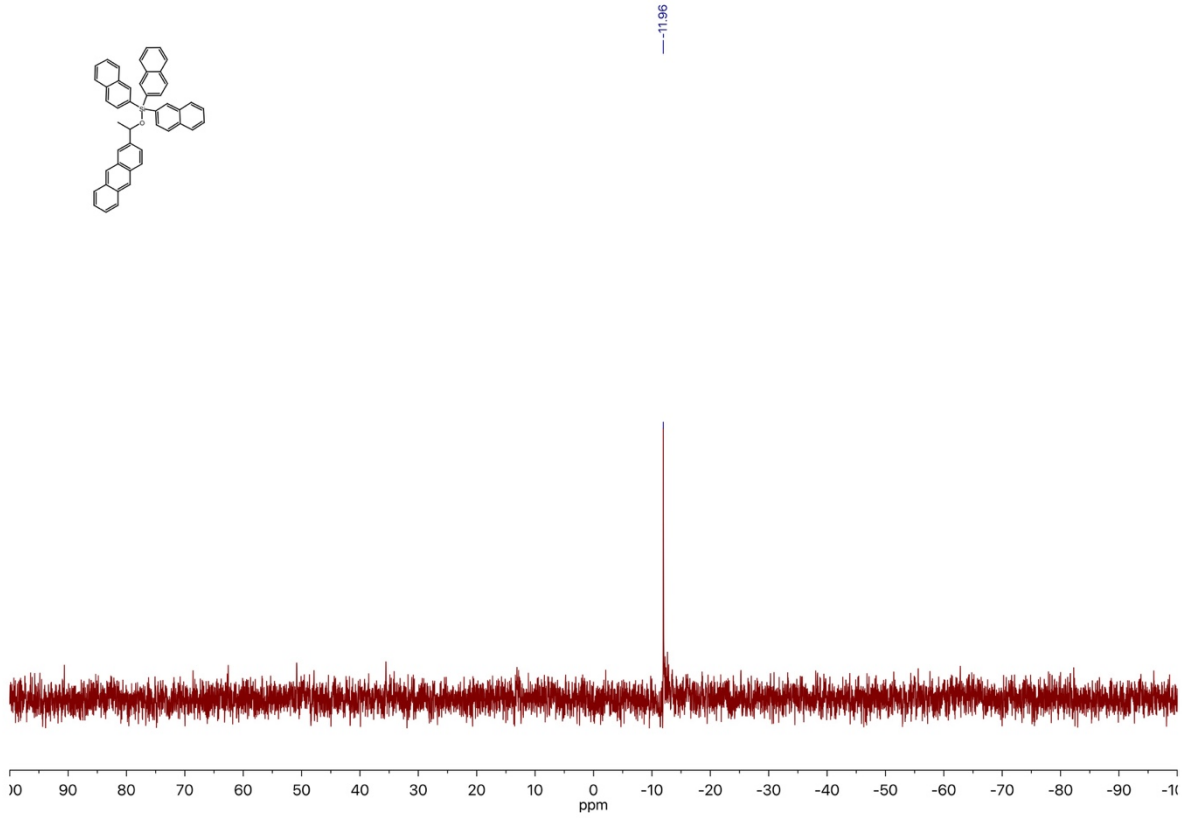


Figure S120: ^{29}Si NMR spectrum of silyl ether **5ee** (79 MHz, $CDCl_3$).

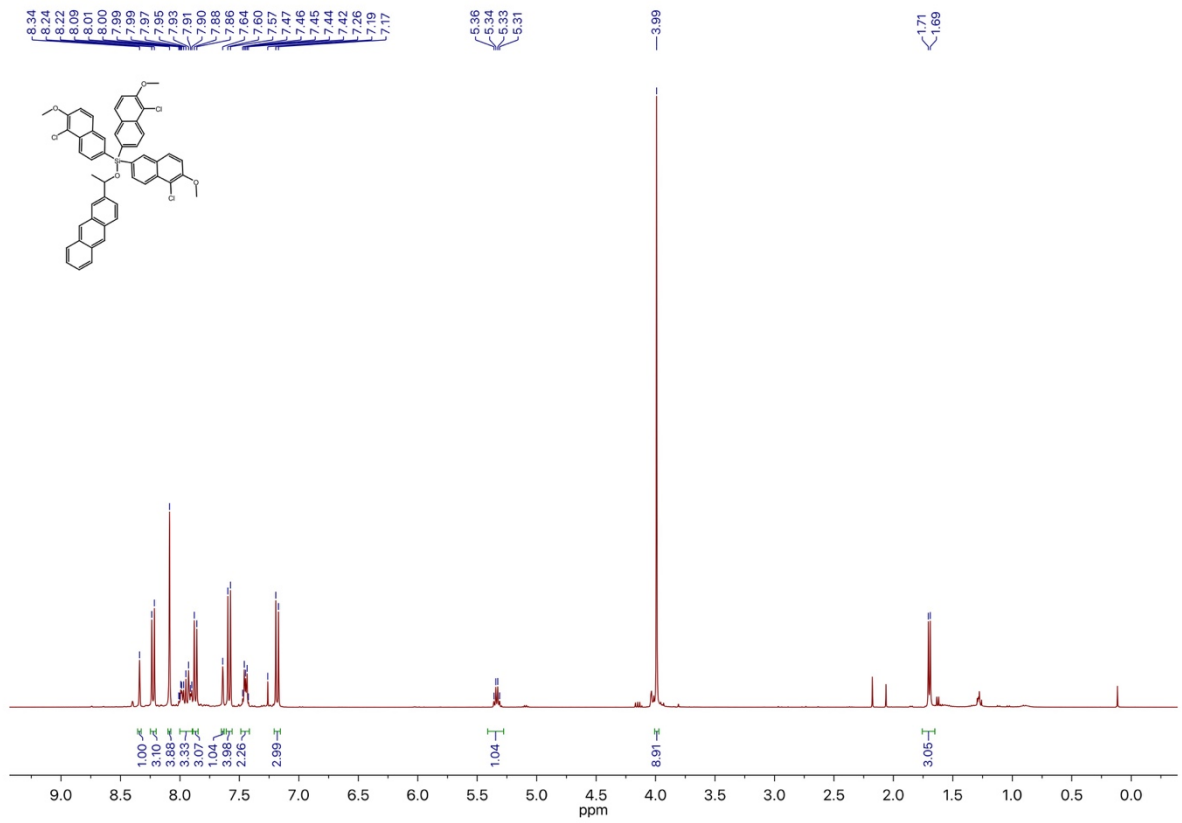


Figure S121: ^{1}H NMR spectrum of silyl ether **5ef** (400 MHz, $CDCl_3$).

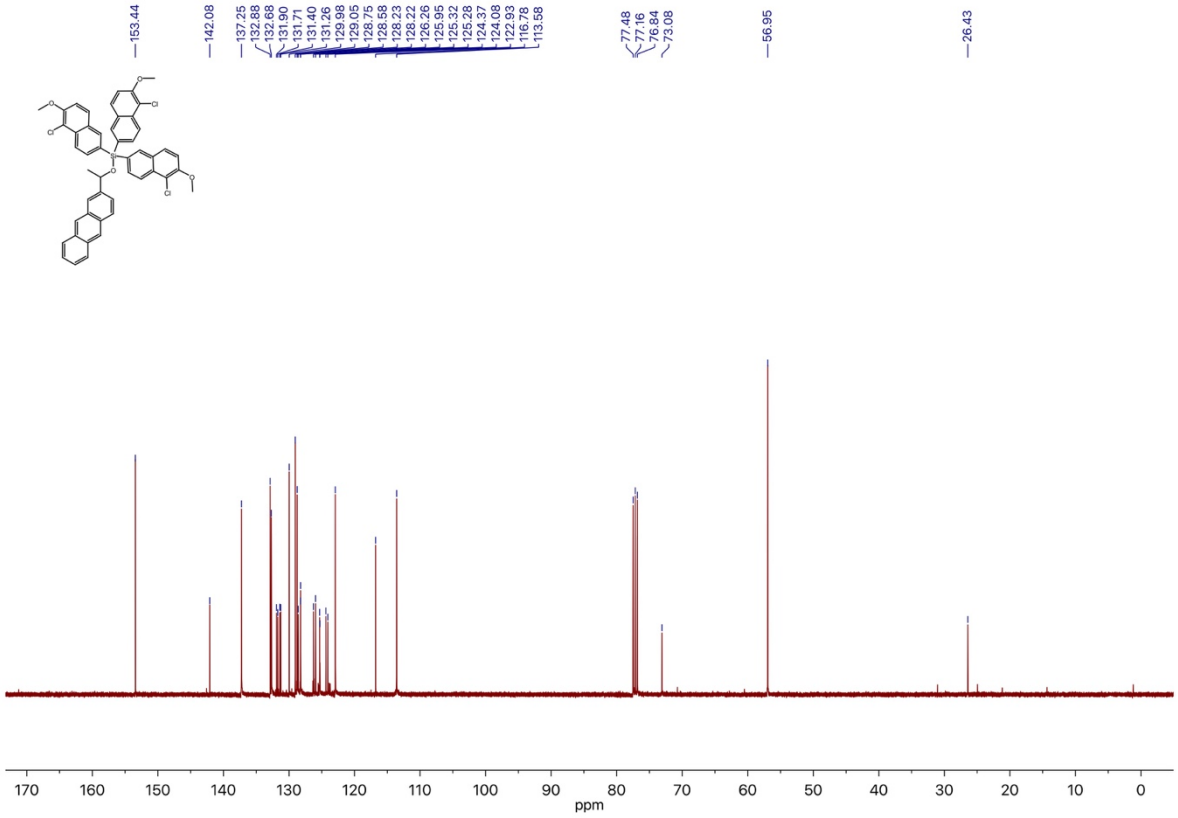


Figure S122: ^{13}C NMR spectrum of silyl ether **5ef** (101 MHz, $CDCl_3$).

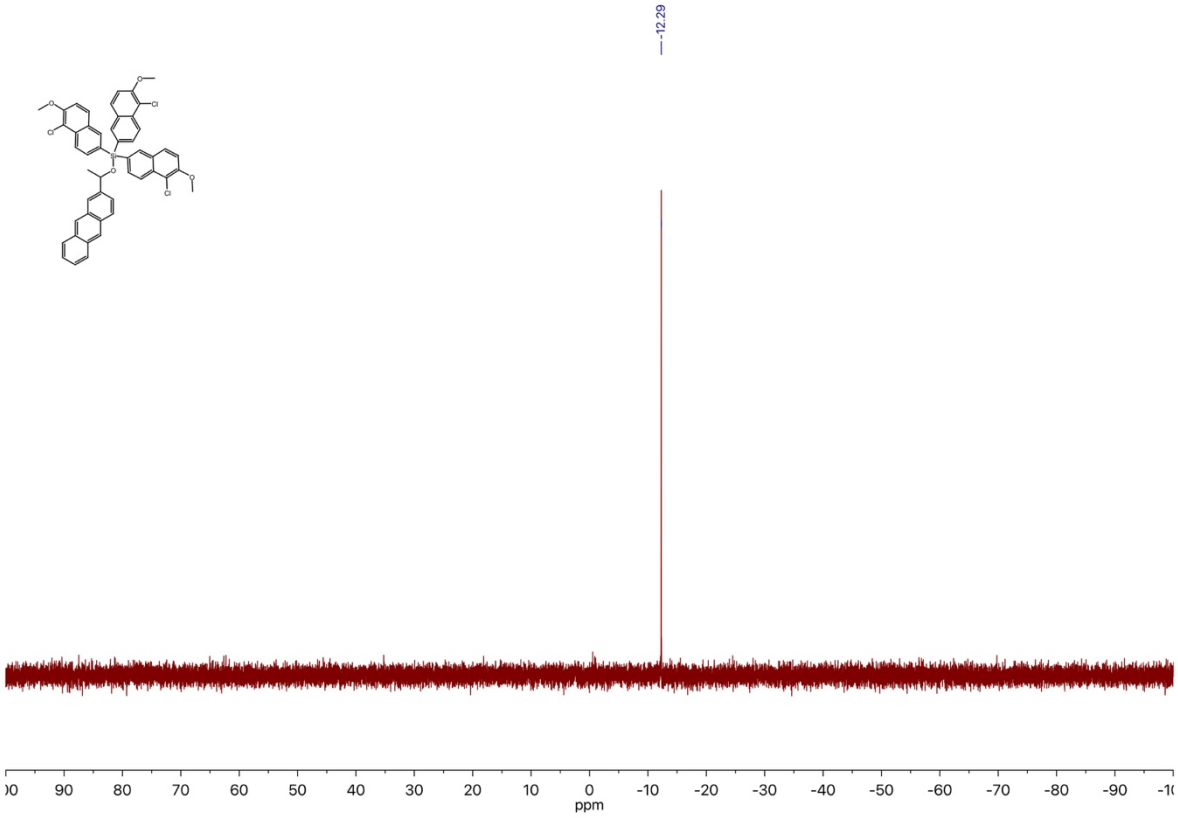


Figure S123: ^{29}Si NMR spectrum of silyl ether **5ef** (79 MHz, $CDCl_3$).

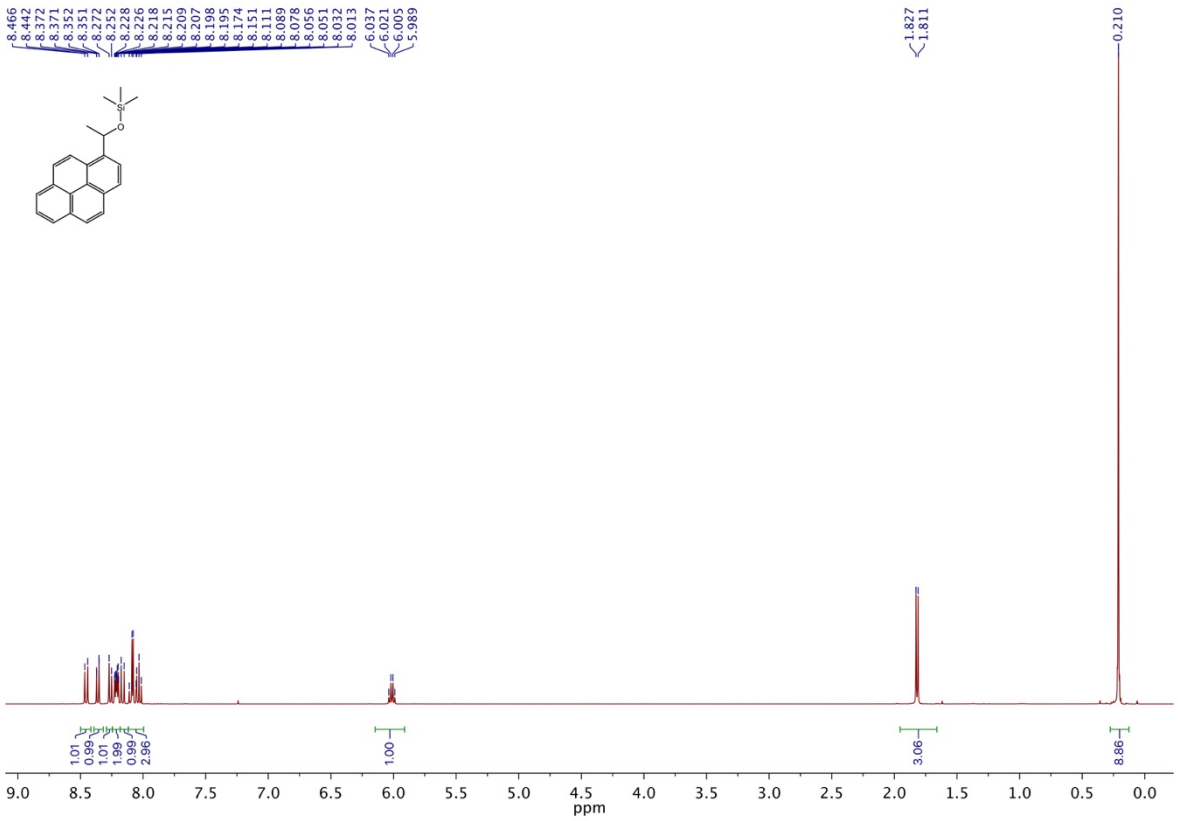


Figure S124: ^{1}H NMR spectrum of silyl ether **5fa** (400 MHz, $CDCl_3$).

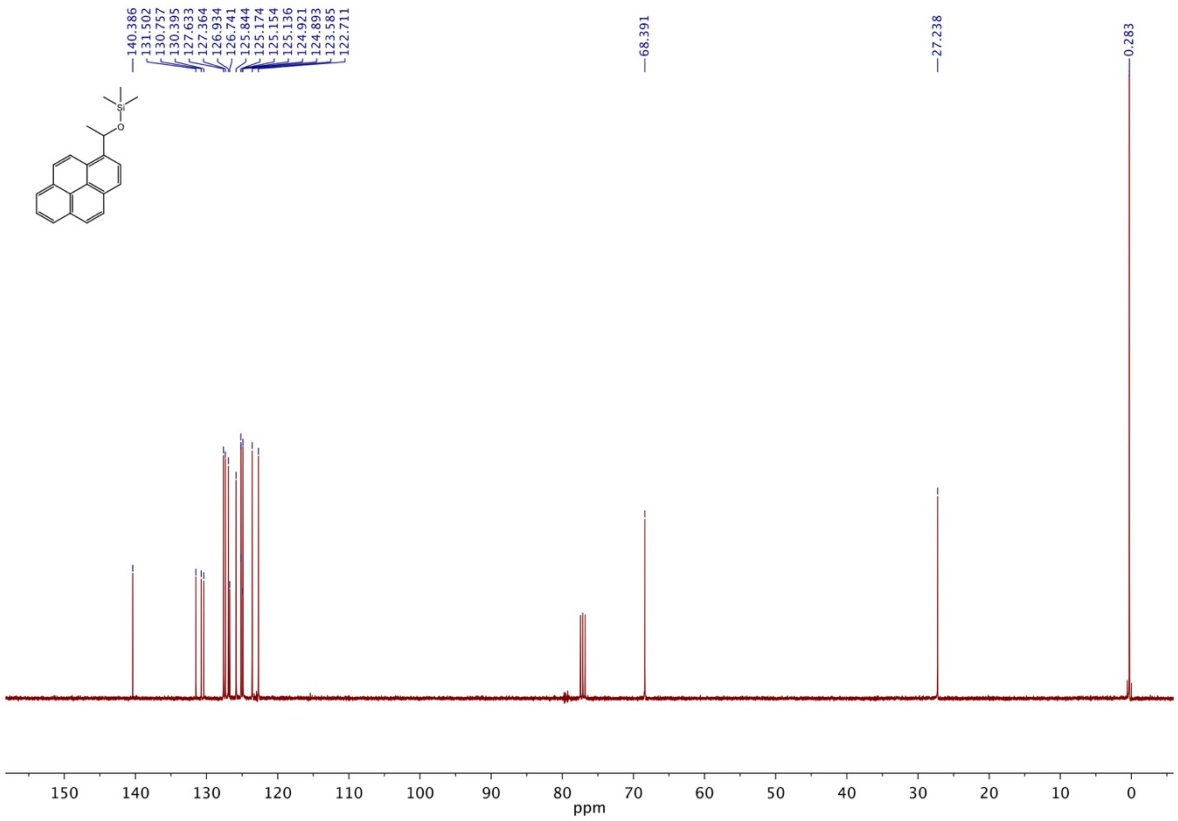


Figure S125: ^{13}C NMR spectrum of silyl ether **5fa** (101 MHz, $CDCl_3$).

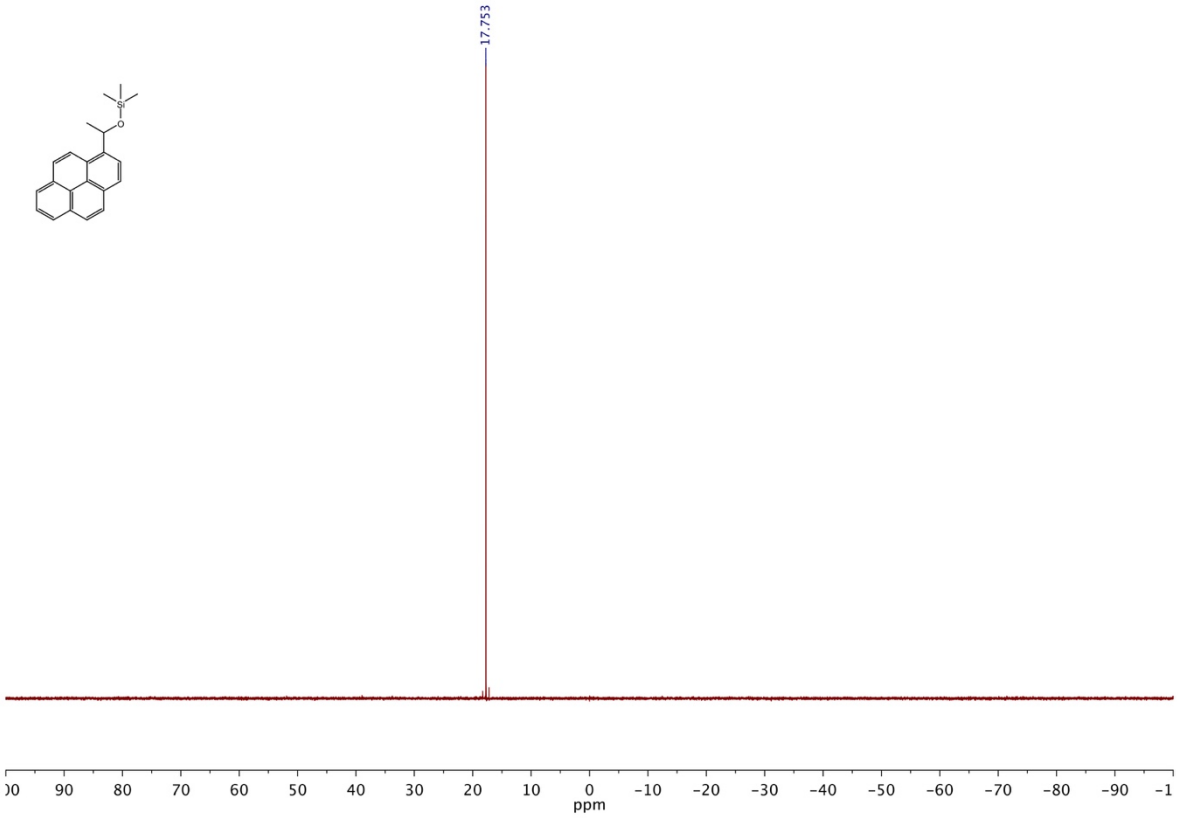


Figure S126: ^{29}Si NMR spectrum of silyl ether **5fa** (79 MHz, $CDCl_3$).

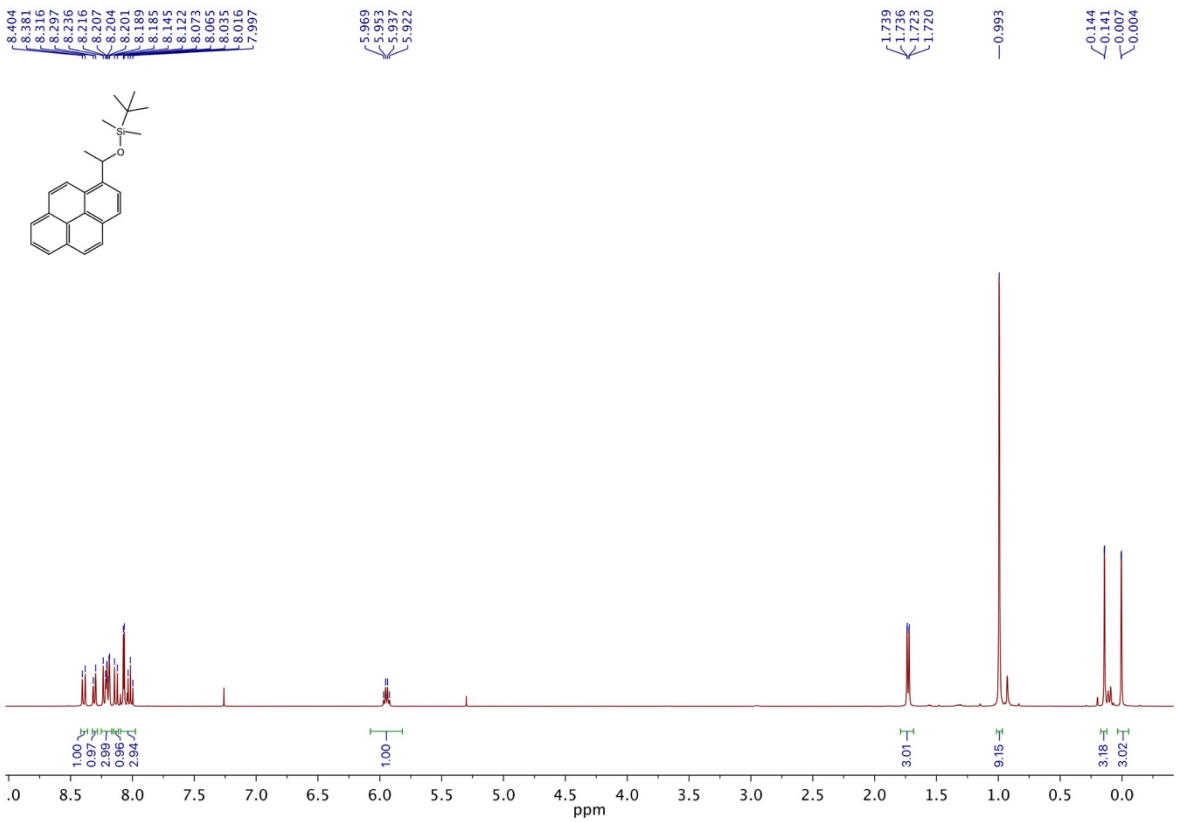


Figure S127: ^{1}H NMR spectrum of silyl ether **5fb** (400 MHz, $CDCl_3$).

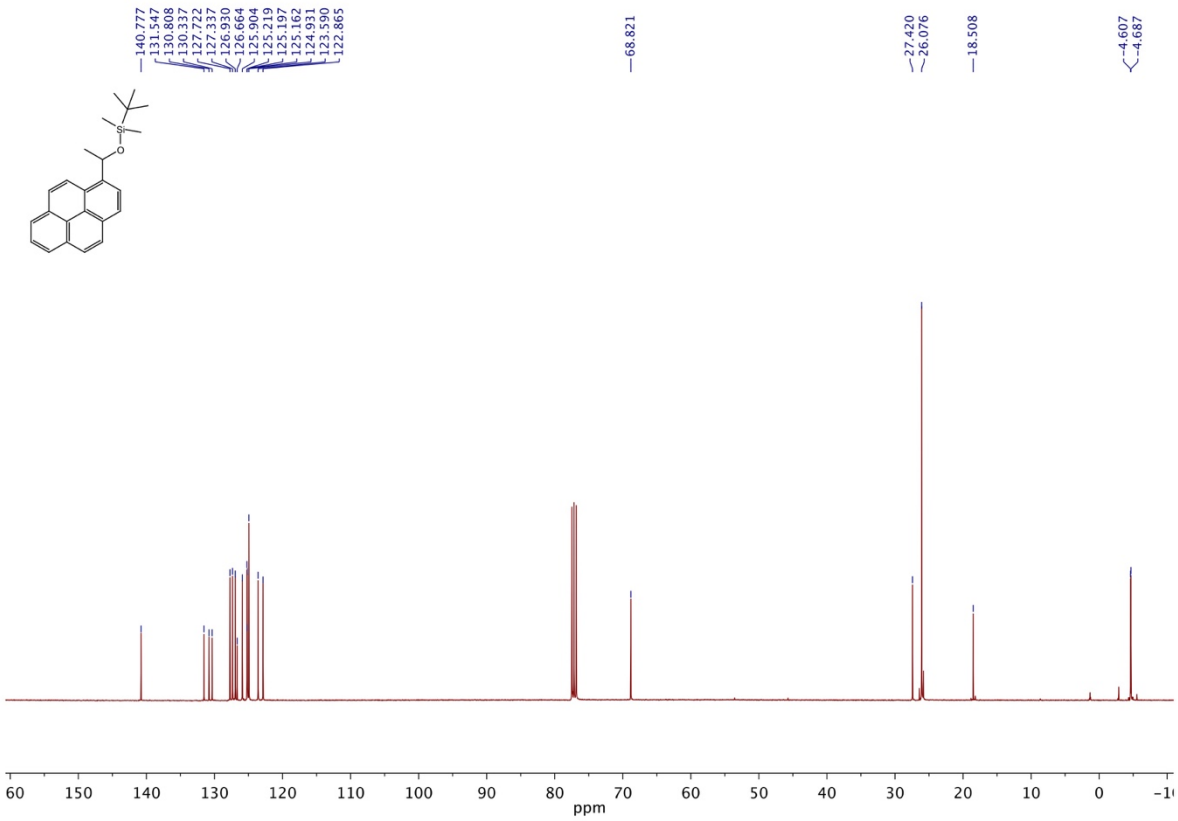


Figure S128: ^{13}C NMR spectrum of silyl ether **5fb** (101 MHz, $CDCl_3$).

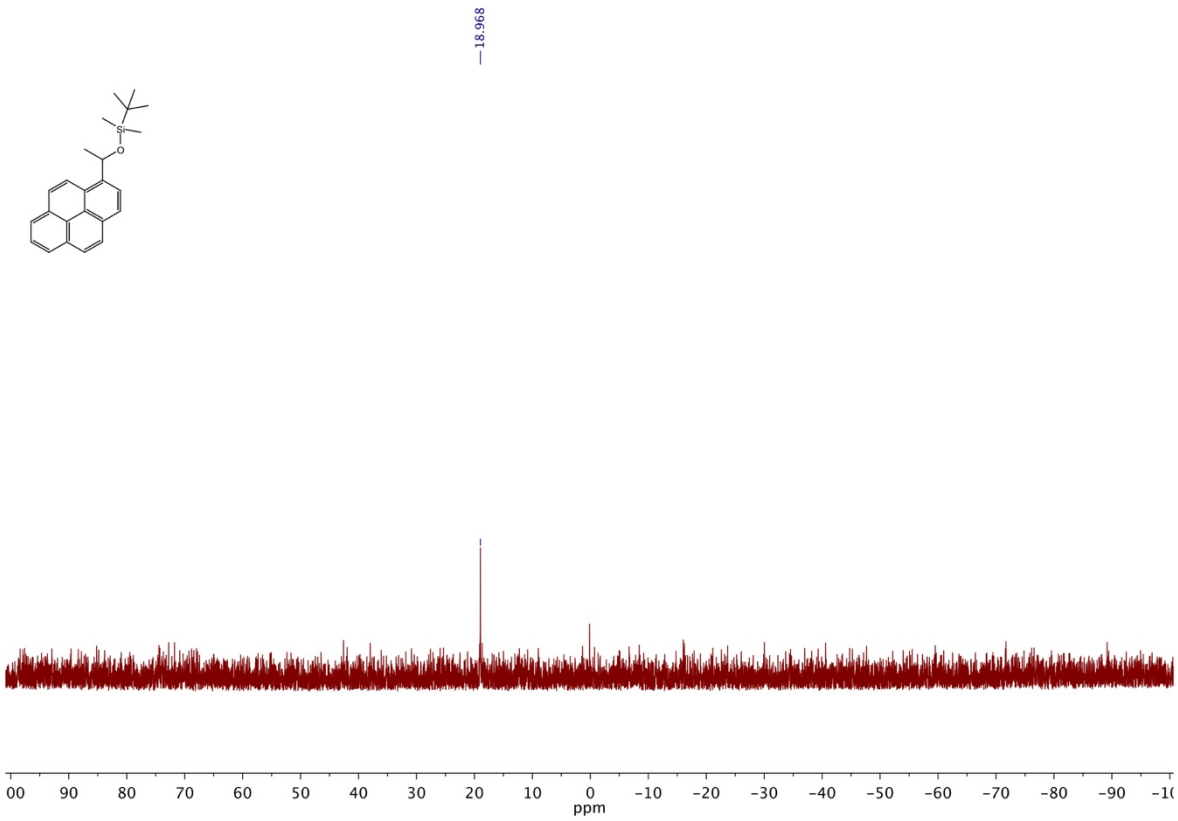


Figure S129: ^{29}Si NMR spectrum of silyl ether **5fb** (79 MHz, $CDCl_3$).

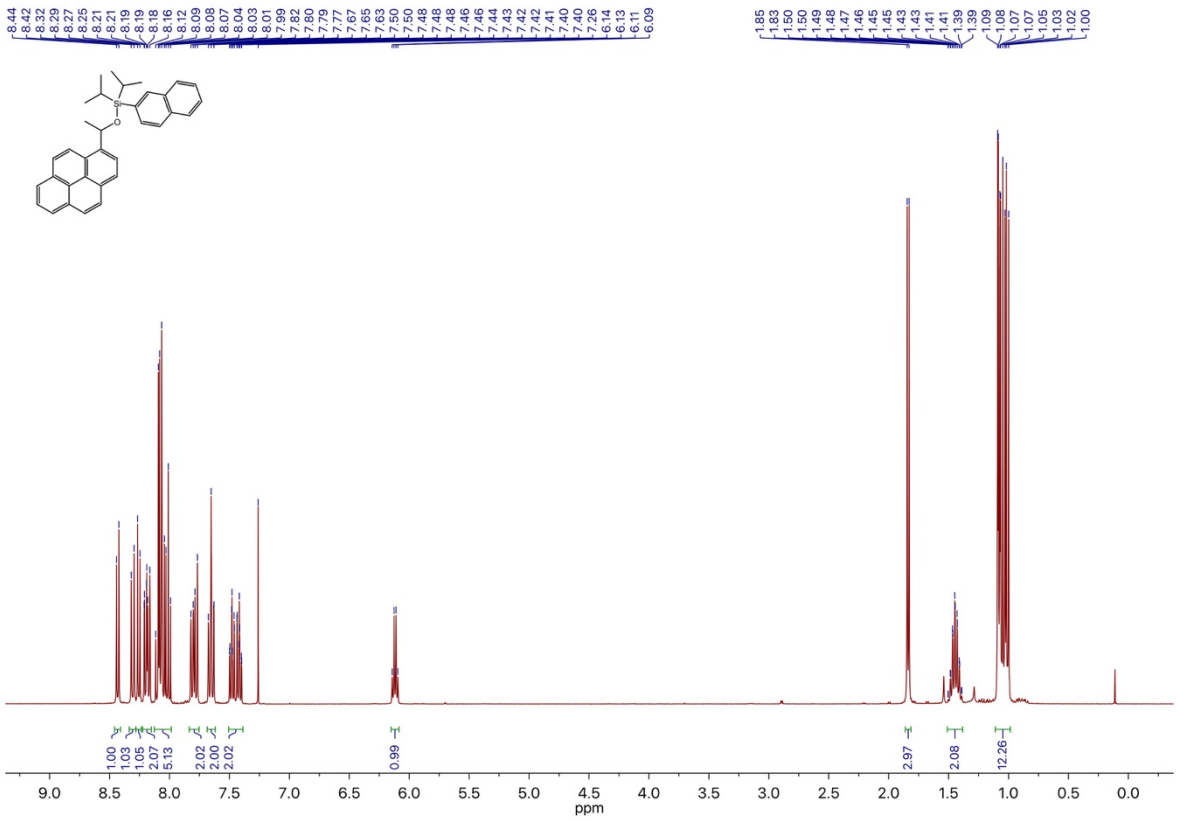


Figure S130: ^{1}H NMR spectrum of silyl ether **5fc** (400 MHz, $CDCl_3$).

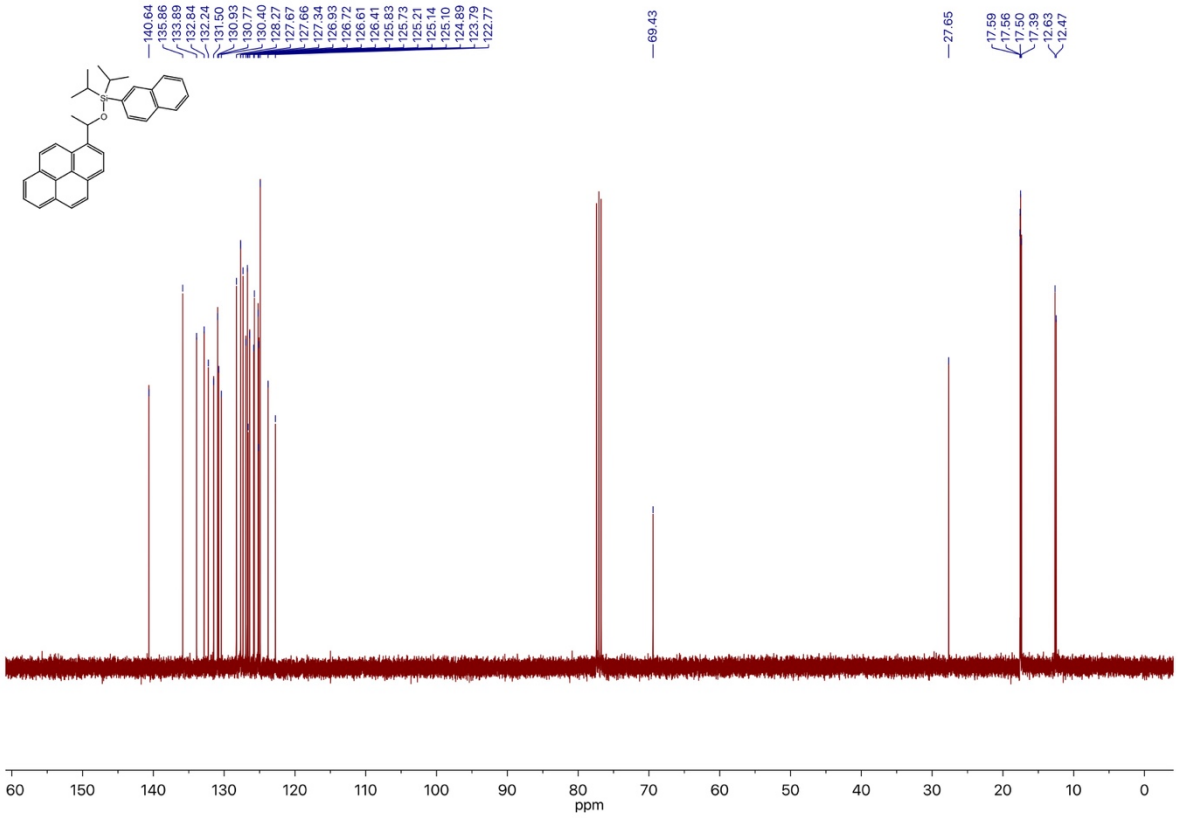


Figure S131: ^{13}C NMR spectrum of silyl ether **5fc** (101 MHz, $CDCl_3$).

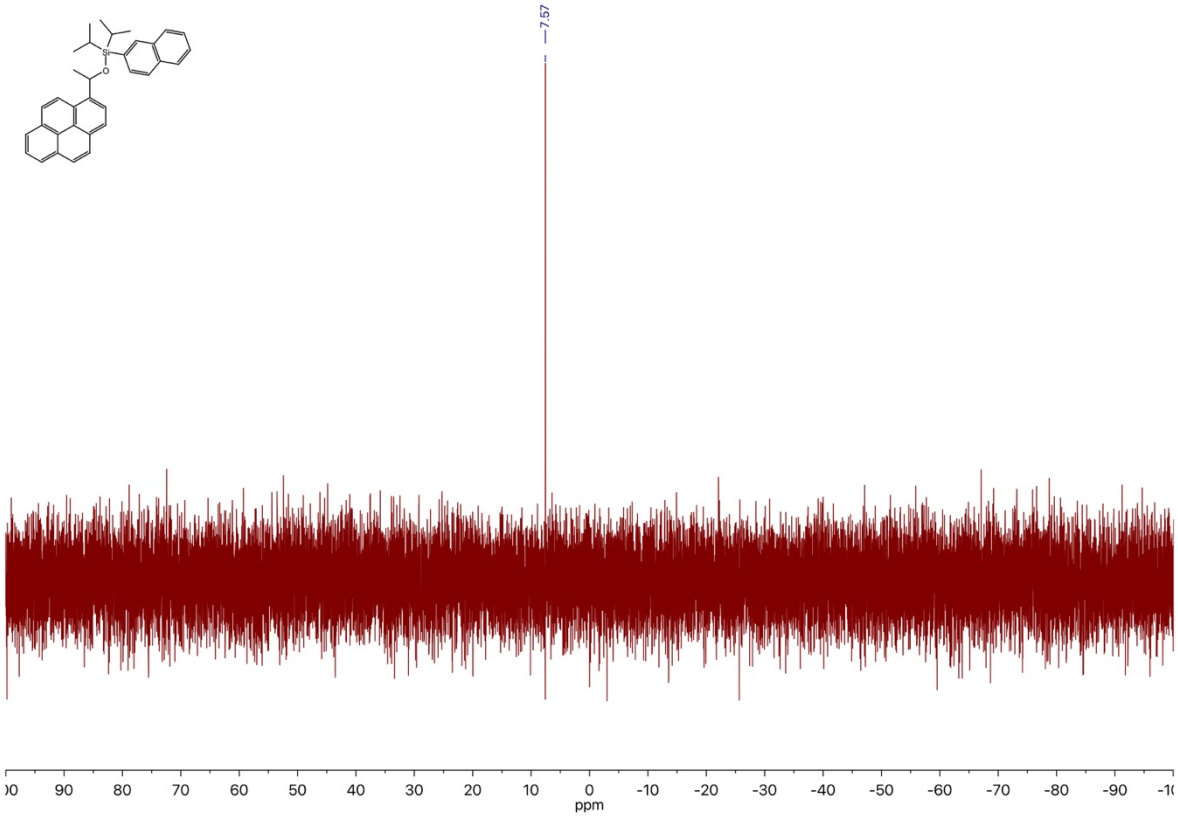


Figure S132: ^{29}Si NMR spectrum of silyl ether **5fc** (79 MHz, $CDCl_3$).

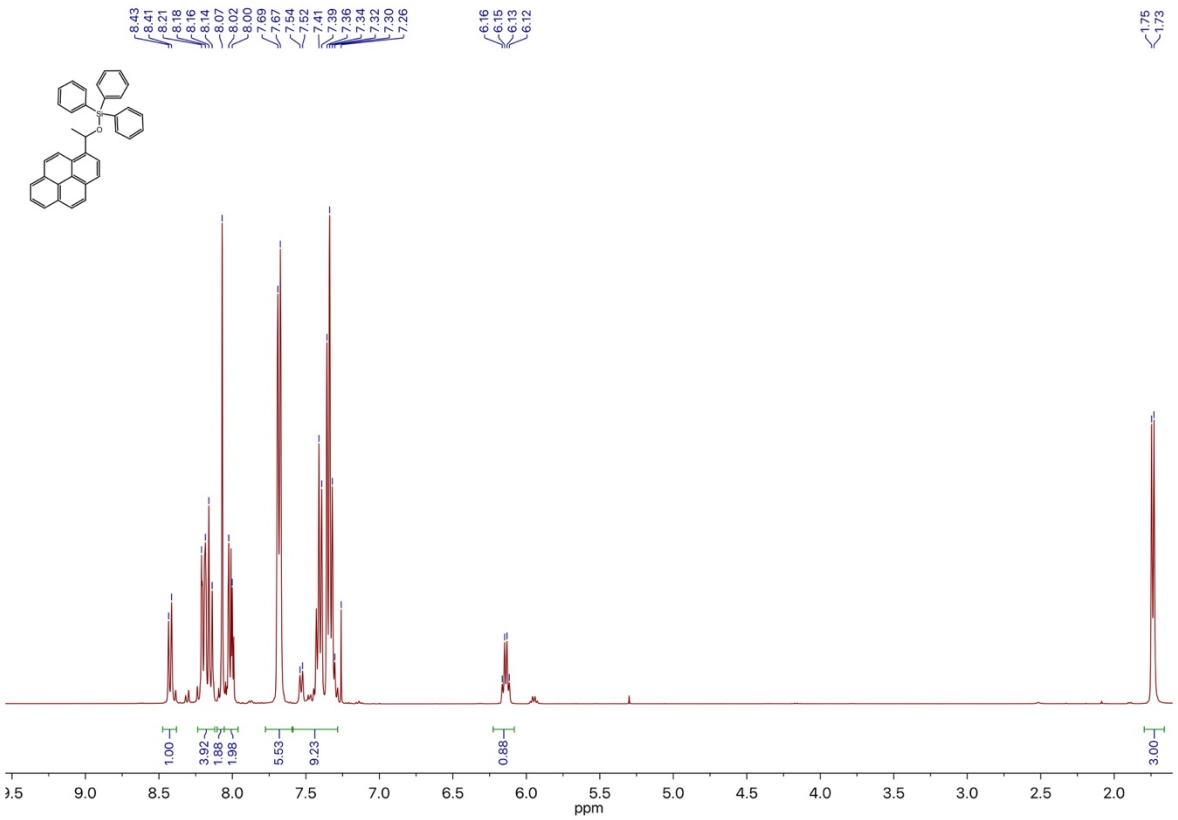


Figure S133: ^{1}H NMR spectrum of silyl ether **5fd** (400 MHz, $CDCl_3$).

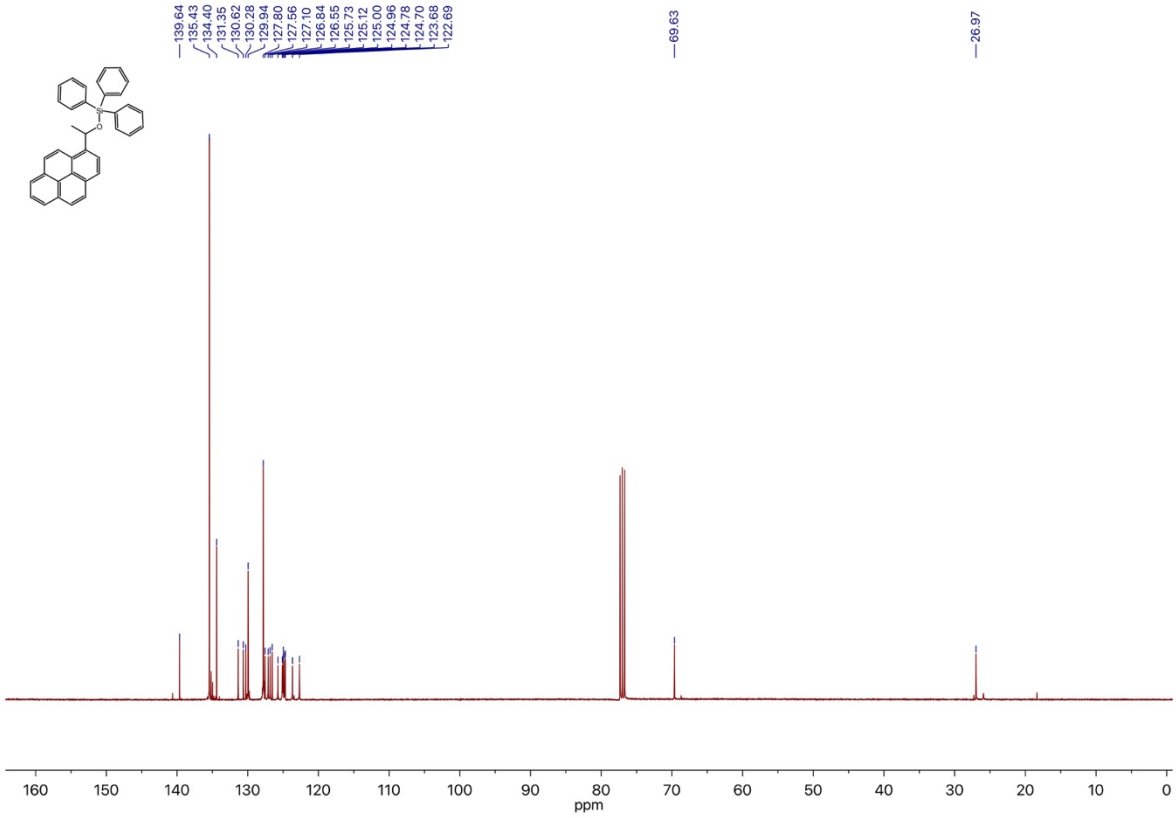


Figure S134: ^{13}C NMR spectrum of silyl ether **5fd** (101 MHz, $CDCl_3$).

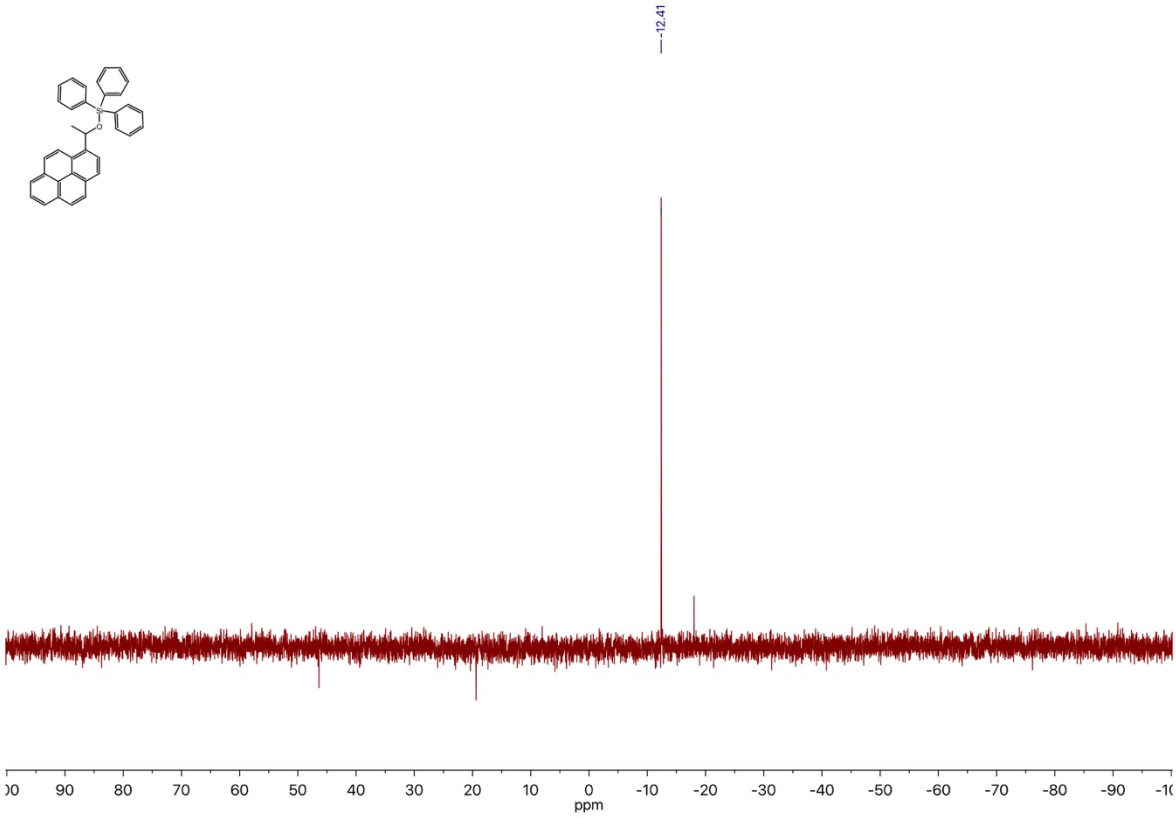


Figure S135: ^{29}Si NMR spectrum of silyl ether **5fd** (79 MHz, $CDCl_3$).

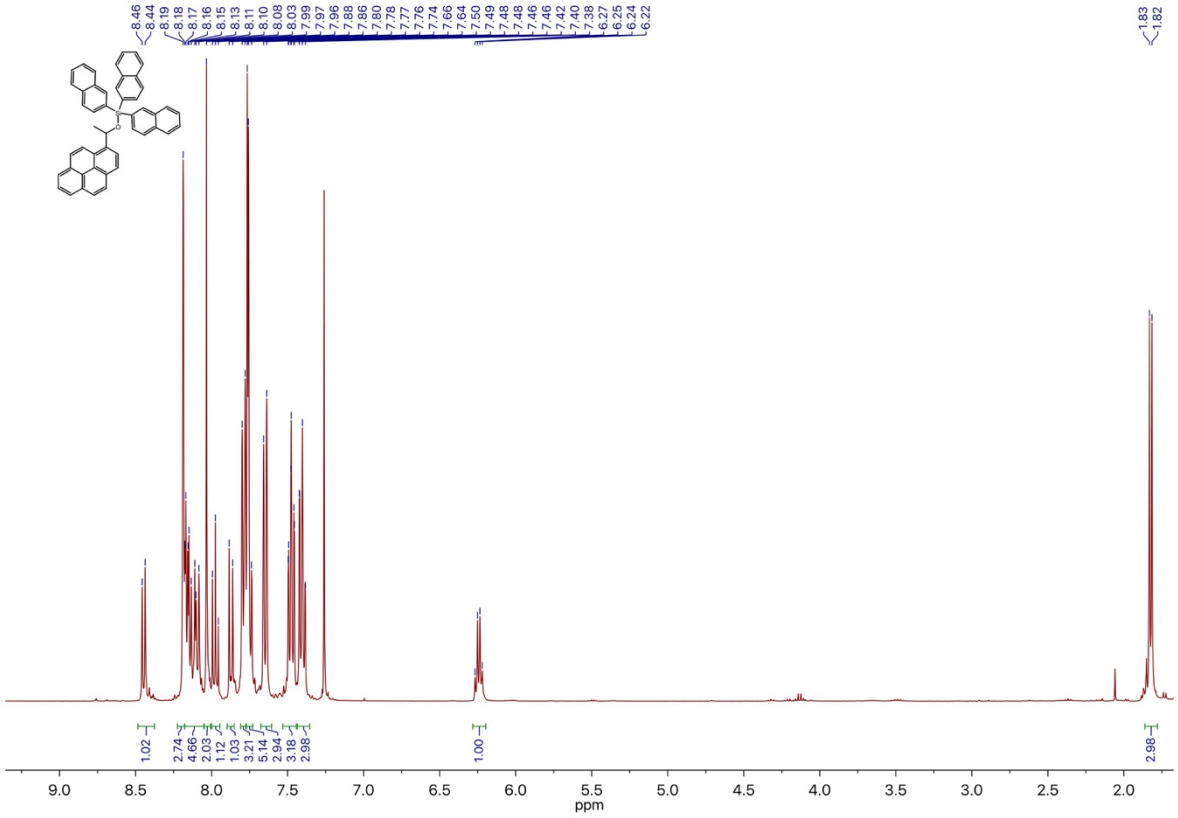


Figure S136: ^{1}H NMR spectrum of silyl ether **5fe** (400 MHz, $CDCl_3$).

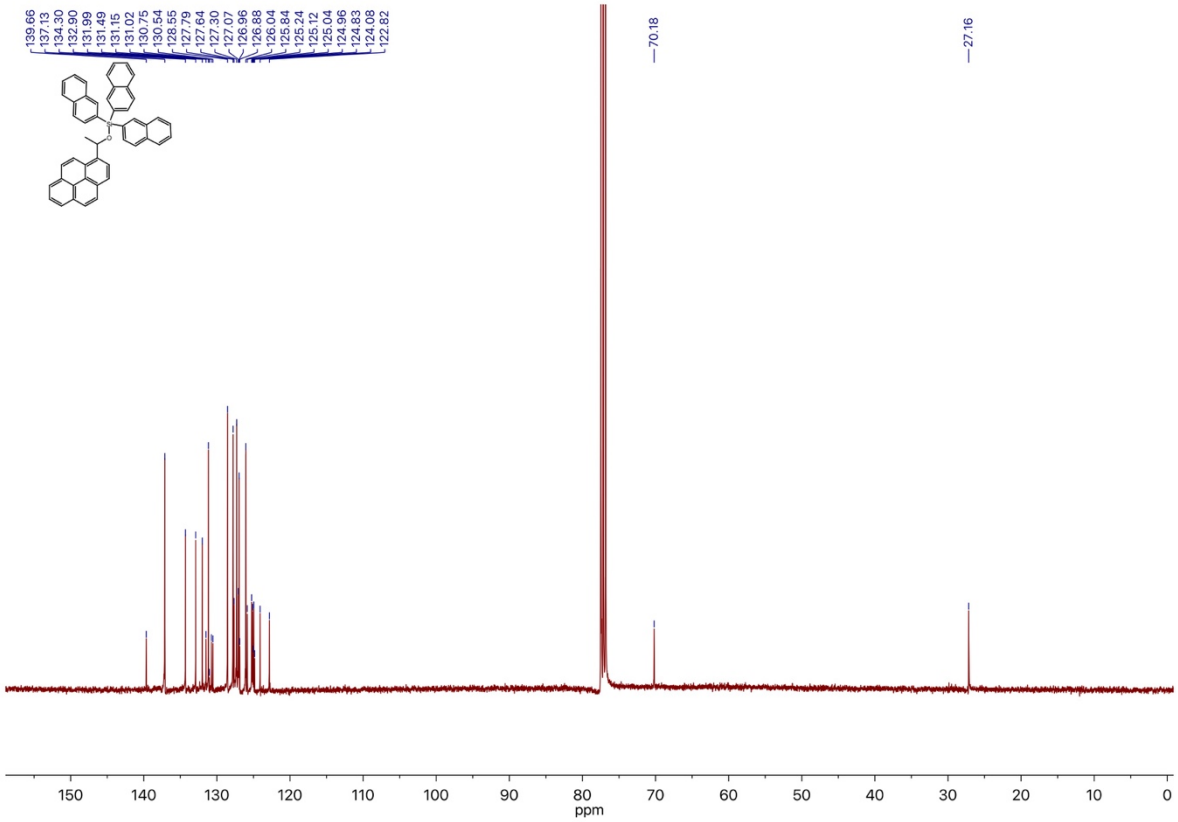


Figure S137: ^{13}C NMR spectrum of silyl ether **5fe** (101 MHz, $CDCl_3$).

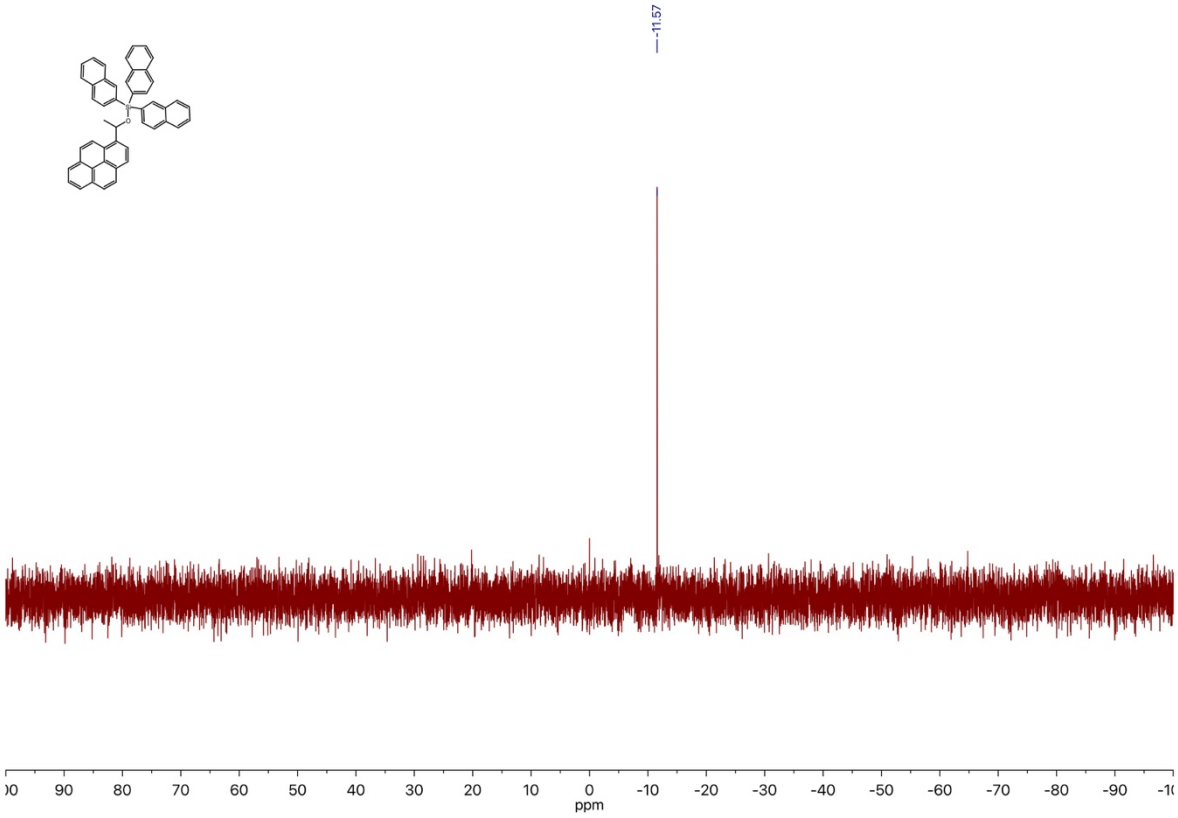


Figure S138: ^{29}Si NMR spectrum of silyl ether **5fe** (79 MHz, $CDCl_3$).

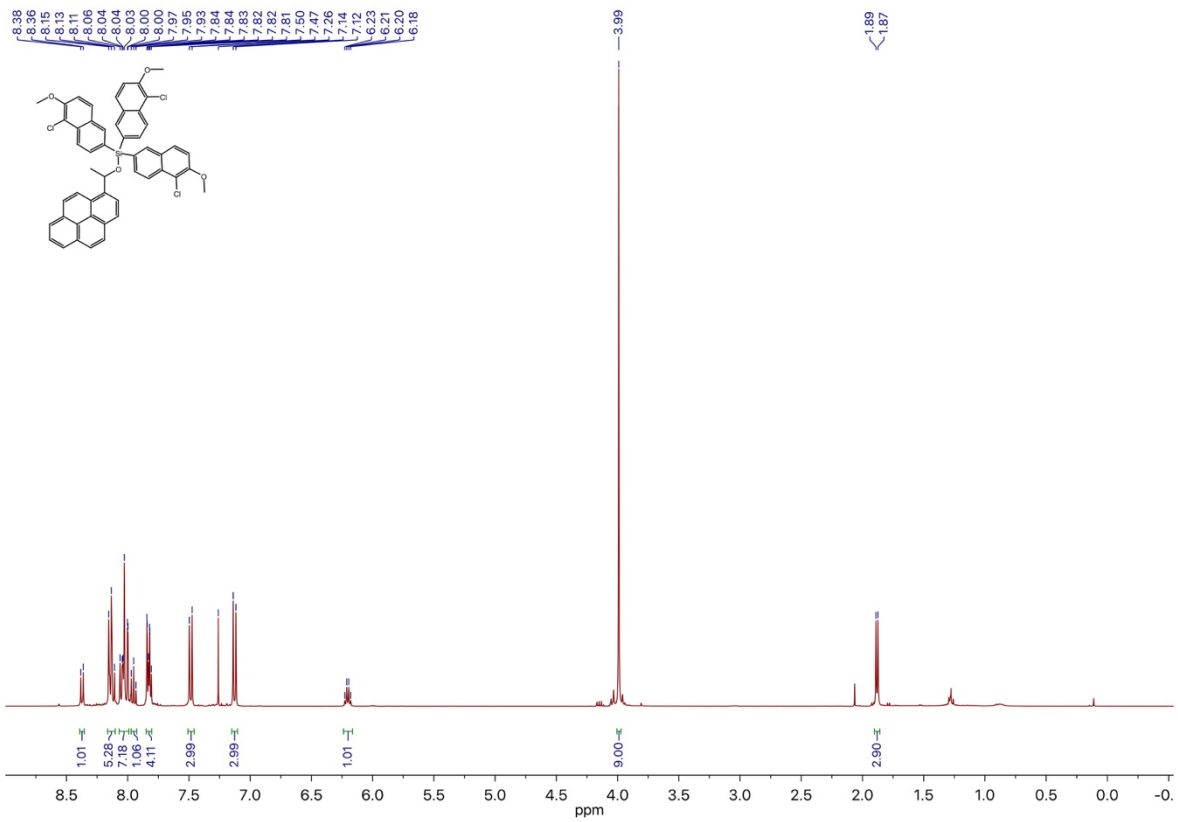


Figure S139: ^{1}H NMR spectrum of silyl ether **5ff** (400 MHz, $CDCl_3$).

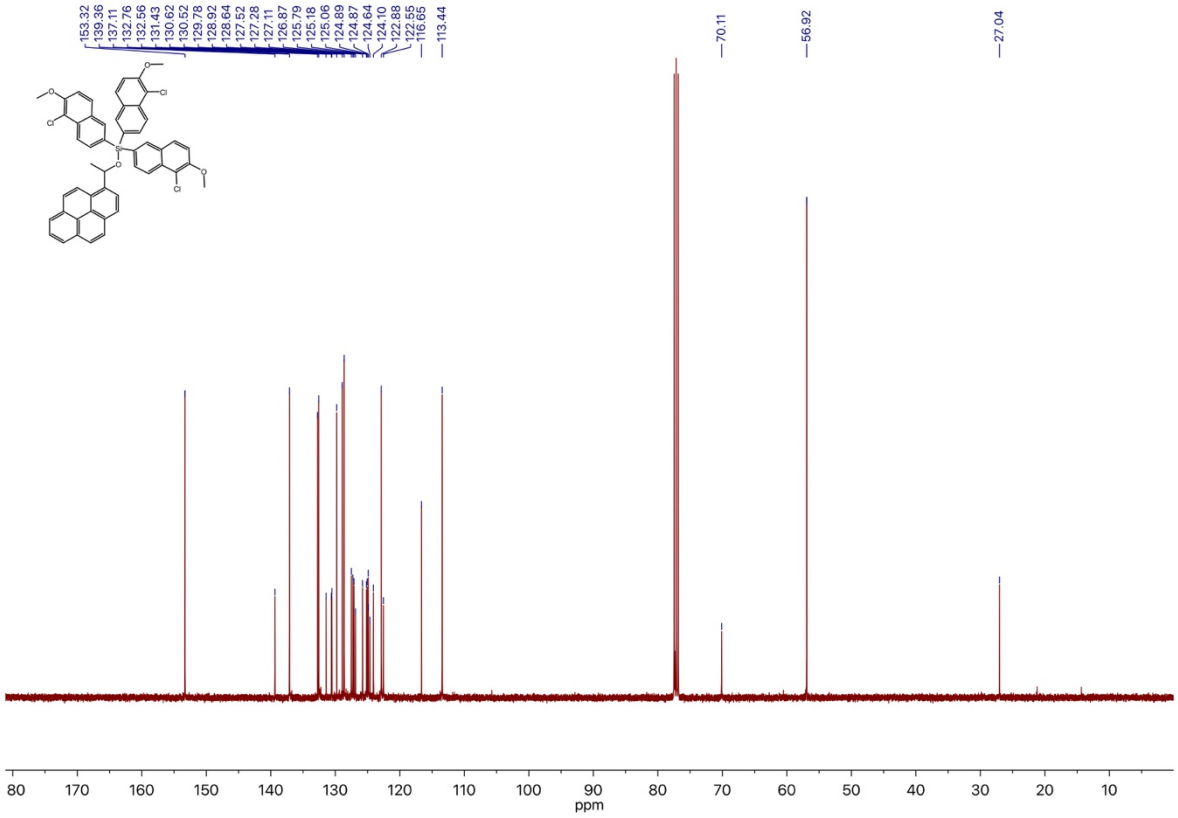


Figure S140: ^{13}C NMR spectrum of silyl ether **5ff** (101 MHz, $CDCl_3$).

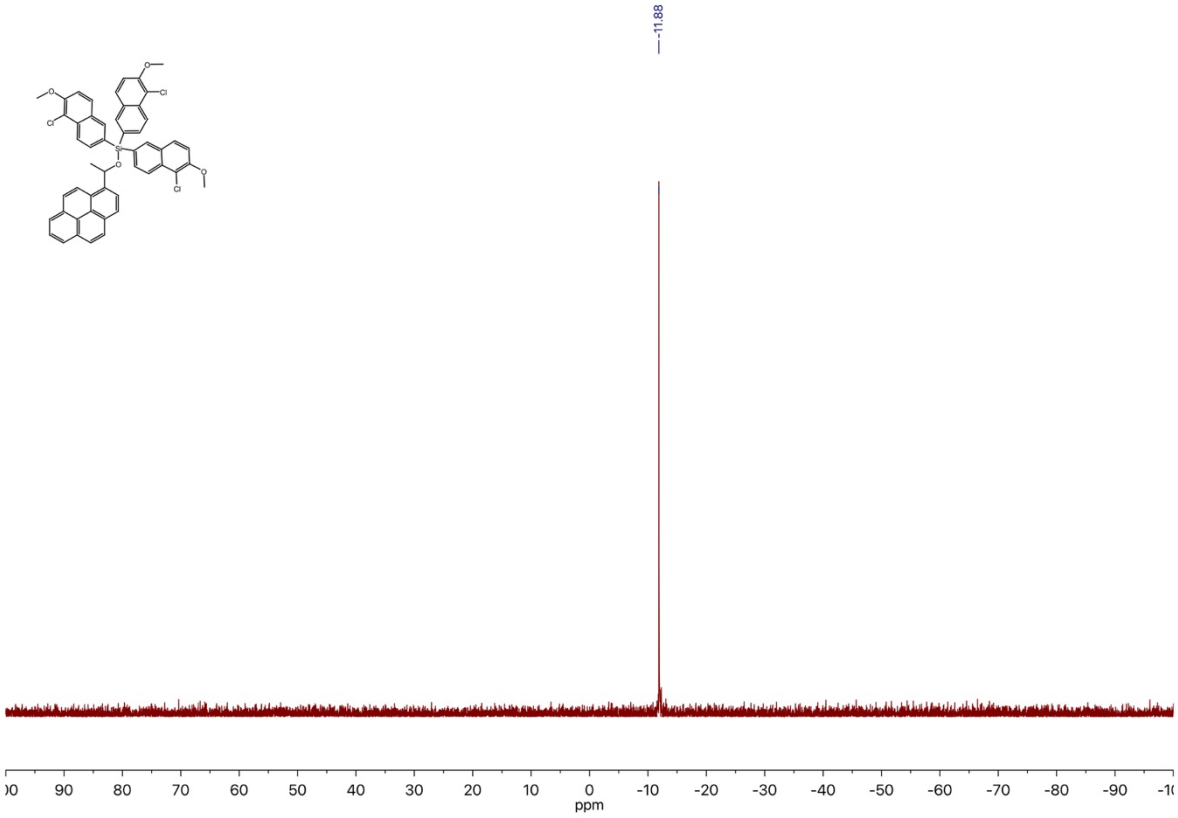


Figure S141: ^{29}Si NMR spectrum of silyl ether **5ff** (79 MHz, $CDCl_3$).

5.4. Crystal Data

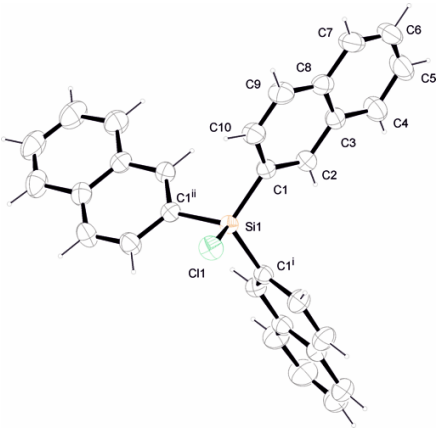


Figure S142: Crystal structure of silyl chloride **2e**.

Table S15: Crystallographic data for silyl chloride **2e.** A small amount of water was found in the crystal that is not shown in the structure. Symmetric codes: i = 1-x+y, 1-x, z; ii = 1-y, x-y, z.

net formula	$C_{30}H_{21.45}ClO_{0.22}Si$
Mr/g mol−1	449.06
crystal size/mm	0.050 × 0.040 × 0.030
T/K	103.(2)
radiation	MoKα
diffractometer	'Bruker D8 Venture TXS'
crystal system	trigonal
space group	'R -3'
a/Å	17.2923(11)
b/Å	17.2923(11)
c/Å	13.9863(10)
α/°	90
β/°	90
γ/°	120
V/Å3	3621.9(5)
Z	6
calc. density/g cm−3	1.235
μ/mm−1	0.224
absorption correction	Multi-Scan
transmission factor range	0.90–0.99
refls. measured	8776
Rint	0.0453
mean σ(I)/I	0.0367
θ range	3.215–26.371
observed refls.	1263
x, y (weighting scheme)	0.0543, 8.1057
hydrogen refinement	constr
refls in refinement	1649
parameters	102
restraints	0
R(Fobs)	0.0481
Rw(F2)	0.1288
S	1.026
shift/errormax	0.001
max electron density/e Å−3	0.433
min electron density/e Å−3	−0.242

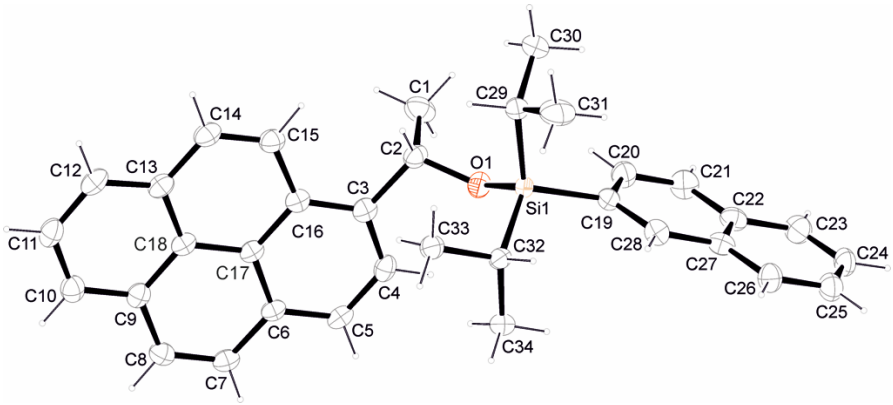


Figure S143: Crystal structure of silyl ether **5fc**

Table S16: Crystallographic data for silyl ether **5fc**.

net formula	$C_{34}H_{34}OSi$
M_r/g mol^{-1}	486.70
crystal size/mm	0.090 × 0.060 × 0.040
T/K	103.(2)
radiation	MoKα
diffractometer	'Bruker D8 Venture TXS'
crystal system	monoclinic
space group	'P 1 21/c 1'
a/Å	10.8826(4)
b/Å	34.7232(14)
c/Å	7.2800(3)
α/°	90
β/°	104.291(2)
γ/°	90
V/Å^3	2665.83(18)
Z	4
calc. density/g cm^{-3}	1.213
μ/mm^{-1}	0.113
absorption correction	Multi-Scan
transmission factor range	0.96–0.99
refls. measured	27642
R_{int}	0.0447
mean σ(I)/I	0.0332
θ range	3.270–26.372
observed refls.	4681
x, y (weighting scheme)	0.0488, 2.9375
hydrogen refinement	constr
refls in refinement	5445
parameters	330
restraints	0
$R(F_{obs})$	0.0551
$R_w(F^2)$	0.1373
S	1.078
shift/error$_{max}$	0.001
max electron density/e Å^{-3}	0.772
min electron density/e Å^{-3}	–0.277

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